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Sewage sludge pyrolysis for liquid production: A review

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ABSTRACT

The high output of sewage sludge, which is increasing during recent years, and the limitations of the existing means of disposing sewage sludge highlight the need to find alternative routes to manage this waste. Biomass and residues like sewage sludge are the only renewable energy sources that can provide C and H, thus it is interesting to process them by means of treatments that enable to obtain chemically valuable products like fuels and not only heat and power; pyrolysis can be one of these treatments. The main objective of this review is to provide an account of the state of the art of sewage sludge pyrolysis for liquid production, which is under study during recent years. This process yields around 50 wt% (daf) of liquid. Typically, this liquid is heterogeneous and it usually separates into two or three phases. Some of these organic phases have very high gross heating values, even similar to those of petroleum-based fuels. The only industrial sewage sludge pyrolysis plant operated to date is currently closed due to some technical challenges and problems of economic viability.

Contents

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1. Introduction

1.1. The problematic disposal of sewage sludge

Sewage sludge is the major waste generated in the urban wastewater treatment process. The implementation of the urban wastewater treatment Directive (UWWTD) 91/271/EEC [1], which obliges Member States to provide a wastewater treatment plant in all agglomerations of more than 2000 population equivalents that discharge their wastewater into a river and in all those of more than 10,000 population equivalents that spill their wastewater into the sea, has caused an important increase in sewage sludge production in the last decade. Specifically, in the EU more than 10 million tons (dry solids) of sewage sludge are produced annually [2]. As an illustration, the evolution of the production of urban in some European countries during recent years is shown in Table 1 [3]. The management of sewage sludge is consequently one of the most significant challenges in wastewater management [4]. Indeed, the urban wastewater treatment process will only be considered completed when sewage sludge, which includes most organic water contaminants, is properly managed in an environmentally friendly manner [5].

1.2. The need for valorization alternatives

Nowadays, the main ways of disposing of sewage sludge can be classified in three categories: agricultural use, incineration, and landfill.

As Directive 75/442/EEC [6] and Directive 91/156/EEC [7] on waste establish, the last option for sludge management should be landfill disposal. The Landfill Directive 99/31/EEC [8] aims to reduce the quantity of biodegradable municipal waste to 35% of that landfilled in 1995 by 2016. Sludge production accounts for about 4% (in weight) of total municipal waste production, therefore its reuse contributes to achieving the target of Directive 99/31/EEC [8]. Besides, sludge contains an elevated amount of organic matter, which generates a landfill gas rich in CH_4 that contributes even more than CO_2 to the greenhouse effect. Moreover, the cost of the land needed for landfill is increasing because of its decreasing availability [9].

The incineration of sludge, which can be performed with and without energy recovery, has several benefits. It can reduce waste volume by 70% and it results in the thermal destruction of pathogens and toxic organic compounds [4,10]. Furthermore, sludge has a calorific value similar to that of low-grade coal so that if incineration is performed under energy recovery conditions, fossil fuel savings would be possible. Another advantage of this disposal method is that the net CO_2 addition to the atmosphere decreases, thus contributing to overall CO_2 reduction. However, incineration is currently considered a high cost alternative [11]. Sludge incineration must comply with Directive 2000/76/EEC [12] on waste incineration which states that the emissions should not exceed permitted levels. The introduction of new technologies to control gaseous emissions has enabled compliance with the legislation but increased costs are also likely. The main scenarios of such incineration are the combustion of sewage sludge in wastewater treatment plants, the co-combustion of sewage sludge with coal or other wastes, or the combustion of sewage sludge in cement kilns [13]. Relatively few incinerators of sewage sludge located in wastewater treatment plants recover the energy from the process, and this causes huge amounts of energy waste [14]. Currently, co-incineration with other waste such as domestic refuse or coal is gaining increasing importance over mono-incineration in the waste water treatment plant itself. However, some authors who have evaluated sewage sludge ash toxicity claim that the ash from the co-combustion of coal and sewage sludge contains larger quantities of metals, namely Cr, Cu, Ni, Pb, Zn and Fe, and is more toxic than the ash from coal combustion [15]. Furthermore, the reuse of the ash generated during incineration is another issue that has to be addressed. The incineration of sewage sludge in cement kilns could solve the problem of ash disposal [16,17]. However, the main obstacle to the complete development of sewage sludge incineration as a route for its management is the poor public perception of this method as a disposal alternative.

Finally, the third and most extensively used disposal method for managing sludge is agricultural use. Due to the technology utilized in urban wastewater treatment, the sludge contains organic matter, nitrogen and phosphorus, which are nutrients for soils. These components make the sludge suitable as a fertilizer. However, the sludge also concentrates heavy metals, pathogens, and

Table 1
Evolution of the production of urban in some European countries during recent years [3].

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Belgium	–	–	101	112	118	109	116	113	128	129	140	–
Bulgaria	52	60	48	45	40	43	58	42	38	40	43	39
Czech Republic	186	198	207	206	211	180	179	172	175	172	220	–
Denmark	154	–	–	–	–	–	–	–	–	140	–	–
Germany	2482	–	–	2429	–	–	2261	2170	2049	–	–	–
Estonia	–	–	–	–	–	–	–	30	28	29	22	22
Ireland	–	38	34	38	–	–	–	60	–	88	–	–
Greece	–	–	–	68	78	80	83	117	126	134	136	152
Spain	716	785	853	892	987	1012	1092	1121	1065	1153	1156	1205
France	971	–	–	954	–	–	1060	–	–	–	1087	–
Italy	–	–	–	–	–	–	–	1056	–	–	–	–
Cyprus	–	–	–	–	–	–	9	8	–	8	–	–
Latvia	–	–	–	–	21	29	36	29	24	23	–	–
Lithuania	486	535	257	242	–	–	–	66	71	76	54	50
Luxembourg	–	17	12	12	13	13	14	13	15	16	13	–
Hungary	87	87	102	115	117	152	184	–	–	260	–	–
Malta	–	–	0	0	0	0	0	0	0	0	0	1
Netherlands	358	372	346	358	365	353	354	359	373	353	353	–
Austria	212	–	315	–	323	–	305	–	255	–	254	–
Poland	340	354	360	397	436	447	476	486	501	533	567	563
Portugal	–	–	–	–	–	–	–	–	–	189	–	–
Romania	–	–	–	–	–	–	–	68	226	100	79	120
Slovenia	7	–	9	8	7	9	10	14	19	21	20	27
Slovakia	54	61	56	53	51	54	53	56	–	–	–	–
Finland	158	160	160	–	–	–	–	–	–	–	–	–
Sweden	221	221	220	220	220	220	210	210	210	217	214	212
United Kingdom	1058	–	–	1527	1544	1656	1721	1771	1809	1825	1814	1761
England and Wales	936	1000	937	1399	1394	1512	1578	1598	1647	1664	1654	1607
Scotland	97	–	–	99	113	113	143	140	124	122	122	116
Northern Ireland	25	–	24	29	37	32	–	32	38	38	38	38
Iceland	0	0	1	1	1	1	–	–	–	–	–	–
Norway	–	–	–	–	–	–	–	–	–	–	–	–
Switzerland	200	–	202	–	200	–	205	–	210	–	–	–
Turkey	–	–	–	–	–	–	–	–	–	–	–	–

some organic compounds which could negatively affect the environment. Following article 14 of the UWWTD [1], "Sludge arising from wastewater treatment shall be re-used whenever appropriate", the European Commission encourages the use of sludge in agriculture claiming that its use is harmless for the environment, while Directive 86/278/EEC [18] regulates this use of sludge to avoid harmful effects. This last Directive limits the heavy metal concentrations in sewage sludge, prohibits the application of untreated sludge unless it is injected or incorporated into the soil, for instance in quarry restoration, and obliges the sludge to be used in such a way that human beings, plants, animals, soils and water are not damaged. Currently, this Directive is under revision to put stricter limits on the use of untreated sludge, the quantity of heavy metals and the concentration of some persistent organic contaminants (PCBs, Dioxins and Furans, PAHs). These contaminants are difficult to break down or eliminate during wastewater treatment and tend to accumulate in the soil, promoting eco-toxicity problems [19]. In this scenario, if sludge quality does not improve, an important percentage of the sludge produced will not be able to be reused as fertilizer in the future [19]. Another drawback of the agricultural use of sludge is the seasonal character of fertilization. Sludge is generated all the year round but it can only be applied on the land once or twice a year. The sludge therefore needs to be stored for long time periods with resulting problems [4,20]. Finally, this reuse also faces social obstacles due to poor public perception. For this reason, the application of sludge on land has decreased or even been abandoned during recent years in several European countries such as Finland, Slovenia, Sweden, Holland, Greece and Belgium [21].

Several authors have compared various alternative disposal routes for sewage sludge [4,13,20,22–25]. However, there is no general agreement on the most appropriate method for sewage sludge management, although the majority opinion is that energy recovery processes will predominate in the near future over other routes such as agricultural use or landfill [4,13,20,23–25]. For example, Stasta et al. [13] and Werther and Ogada [25] recommend its management in cement kilns, Fytili et al. [4] suggest alternative thermal processes such as pyrolysis, gasification or wet oxidation, and Hospido et al. [22] argue for land application. Some authors also emphasize that it is difficult to compare the different kinds of sewage sludge management treatment because some are still at the research stage [23,24]. As can be seen in Fig. 1, the management methods used in European countries is equally heterogeneous [26].

In view of the current situation of disposal routes for sewage sludge as described above, a high demand for new alternative methods of sludge management can be expected in the near future. Lately, thermal processes such as wet oxidation, pyrolysis or gasification have been researched and suggested as potential alternatives [25]. Two earlier reviews cover past and future trends in sludge handling, focusing mainly on thermal processes and the utilization of sewage sludge in cement manufacture as a co-fuel [4,25]. The main goal of thermochemical processes, including combustion, is the production of energy from the organic fraction of the sludge, while affecting the environment as little as possible. The pyrolysis process has considerable potential for sewage sludge management since it achieves up to 50% reduction of the waste volume [27], the stabilization of the organic matter, and the production of fuels and valuable chemical products from the liquid obtained. Apart from this, sewage sludge pyrolysis also enables the heavy metals from the sewage sludge to be concentrated in the char obtained from the pyrolysis, these metals being more resistant to lixiviation than those concentrated in the ash obtained from sewage sludge combustion [28–30]. This solid product may also be used as a reducer in metallurgic processes, as an adsorbent of contaminants or as a fuel to maintain the process [31,32]. Furthermore, unlike other thermochemical processes such as combustion or gasification, pyrolysis

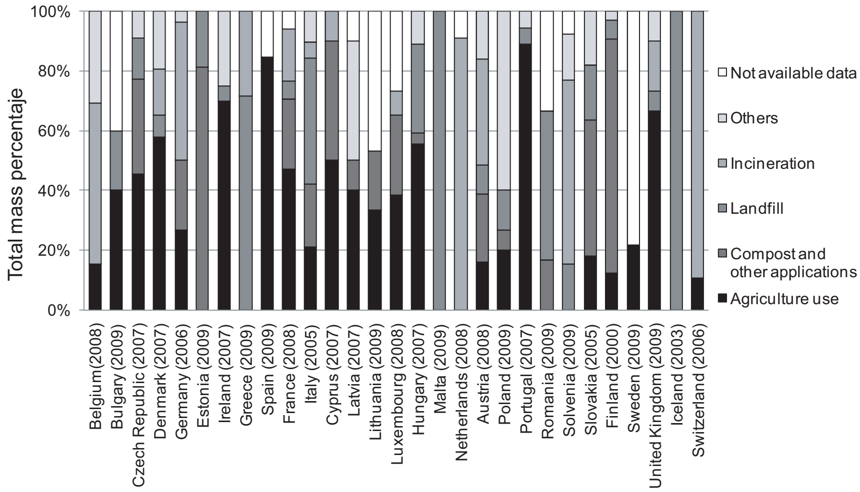


Fig. 1. Sewage sludge disposal by type of treatment (latest available year) [26].

is an endothermic reaction. This means that the pyrolysis products may have a more elevated heating value than the raw material pyrolyzed. For example, Kim and Parker [33] found that the liquid and the solid products of pyrolysis at 300 °C of TWAS (thickened waste activated sludge) had an energy content between 0.16 and 1.9 MJ kg^{-1} more than the raw sewage sludge. However, it must be borne in mind that as the reaction is endothermic, it is necessary to provide external energy to the system for the reaction to take place.

This paper reviews the published research on sewage sludge pyrolysis for liquid production because, to the best of the authors' knowledge, there is no review currently available on this topic. The main objective is to provide an account of the state of the art of sewage sludge pyrolysis for liquid production. Furthermore, based on the data found in the literature review and on the experience of the Thermochemical Processes Group (GPT) within this field, the review will try to establish the most urgent priorities for future investigations required for the complete development of this form of waste management.

1.3. *Pyrolysis: a potential method for sewage sludge management*

Most of the works concerning liquid production from sludge are based on the literature relating to the pyrolysis of lignocellulosic biomass. In fact, important efforts have been made to convert biomass to liquid fuels since the oil crisis in 1970s [34]. Therefore, the information published about this process applied to biomass is vast and provides a basis for the application of pyrolysis to sludge in order to obtain bio-oil. For this reason, before discussing sewage sludge pyrolysis, it is necessary to describe what is meant by pyrolysis and bio-oil and briefly summarize how this process should be performed to obtain liquid fuel according to the experiences gained with wood/biomass pyrolysis.

Pyrolysis is the thermal decomposition of materials in an inert atmosphere producing vapors, which are formed by condensable and non-condensable gases, and a solid product, namely char. It is important to distinguish pyrolysis from gasification. Gasification mainly transforms organic materials to combustible gas or syngas, using between 20 and 40% of the oxygen required for total combustion, whereas pyrolysis is a thermochemical reaction carried out at elevated temperatures (500–1000 °C) and theoretically in an inert atmosphere. Depending on the operational conditions, pyrolysis can be aimed at obtaining mainly char, liquid or gas. A pyrolysis reaction carried out at high heating rates, moderate temperatures (500 °C), short gas residence times (<2 s), and rapid quenching of the vapors is known as fast pyrolysis. The major product obtained in this process is the pyrolysis liquid, also called bio-oil or pyrolysis oil, which can be applied as a fuel and also as a source of valuable chemical products. In the case of lignocellulosic biomass pyrolysis, the yields achieved are 60–75 wt% for the liquid, 15–25 wt% for the char and 10–20 wt% for the gas [34]. Char and gas can also be considered as fuels and be reused in the process itself.

The choice of the reactor configuration is essential in order to meet fast pyrolysis requirements and maximize the liquid production. There are three main kinds of technologies for fast pyrolysis: ablative pyrolysis, fluid bed and circulating fluid bed pyrolysis, and vacuum pyrolysis [35]. Fluid beds are the most popular configurations due to their ease of operation and ready scale-up [35]. In fact, nowadays only fluid beds and circulating fluid beds are being used on a commercial scale [36].

Pyrolysis has the advantage over other thermal treatments of producing mainly a liquid product that can be easily stored and transported and can therefore be used in areas far away from the liquid production plant. Pyrolysis liquid from lignocellulosic biomass has already been successfully tested as a direct fuel in engines, turbines and boilers [37,38]. However, the potential direct substitution of pyrolysis oil for conventional petroleum-based fuels in transport applications requires upgrading processes which are currently being investigated [39].

Pyrolysis oil from lignocellulosic biomass is a liquid which can be considered as a microemulsion of organic macromolecules stabilized in an aqueous solution of smaller organic molecules. Microemulsion stabilization is achieved by hydrogen bonding and nanomicelle and micromicelle formation [40]. The main organic compounds found in the pyrolysis liquid have been classified in five categories: hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids and phenolics compounds [40]. A typical heating value of biomass pyrolysis liquid is around 17 MJ kg^{-1} [34] which is 40–45% of that exhibited by hydrocarbon-based fuels [38]. Two of the main chemical differences between biomass pyrolysis oils and hydrocarbons fuels are water and oxygen content. The water content in pyrolysis oils varies over a wide range (15–30 wt%) depending on the feedstock and the process conditions [38]. High water contents deplete the lower heating value but on the other hand decrease the viscosity, which is beneficial for its applications as a fuel. The oxygen content of pyrolysis liquid is usually 45–50 wt% depending mainly on the liquid water content [41]. The oxygen is present in most of the more than 300 compounds that have been identified in the oils [38]. This high oxygen content reduces energy density and provokes immiscibility

with hydrocarbon-based fuels. It also increases liquid storage and thermal instability due to the reactive oxygen-containing organic compounds present in the pyrolysis oil [38]. This instability is also called aging, which is an undesirable property. These reactive components can interact to form larger molecules and cause changes in physical properties [42], such as water content and viscosity increase, and phase separation. Generally, fresh pyrolysis liquid from clean wood (without bark and needles) forms a stable single-phase and phase separation occurs with aging [43]. However, phase separation can also appear in fresh pyrolysis oils produced from feedstocks with high extractive content, such as forestry residues [44], and/or with high moisture which can generate oils with water content above 35–40 wt% [43].

Since 1986, several authors have studied sewage sludge pyrolysis as a potential method for obtaining a liquid fuel and chemicals [40]. Works relating to wood/biomass pyrolysis have frequently been cited as references for investigations into the production of liquid from sewage sludge pyrolysis. However, the differences in chemical composition between sewage sludge and lignocellulosic biomass involve important changes in the chemical and physical properties of the pyrolysis liquids obtained with each feedstock. This paper seeks to review the work carried out into sewage sludge pyrolysis with an emphasis on producing liquid. Comparisons are sometimes made between sewage sludge and lignocellulosic biomass pyrolysis oils to indicate and discuss the main differences between them.

2. Sewage sludge composition and characteristics

Sewage sludge is a complex heterogeneous mixture of microorganisms, undigested organics such as paper, plant residues, oils, or fecal material, inorganic materials and moisture [45]. The undigested organic materials contain a highly complex mixture of molecules coming from proteins and peptides, lipids, polysaccharides, plant macromolecules with phenolic structures (e.g. lignins or tannins) or aliphatic structures (e.g. cutins or suberins), along with organic micropollutants such as polycyclic aromatic hydrocarbons or dibenzofurans [19]. The inorganic materials present in the liquids come mainly from soil but also from synthetic polymers of anthropogenic origin [2].

The origin, the purification treatment applied to the wastewater (mainly active mud or bacteria beds) and the stabilization and conditioning treatments applied to the sewage sludge affect significantly: (1) the level of decomposition of the organic materials, (2) the presence of certain constituents, such as the inorganic materials deriving from synthetic polymers of anthropogenic origin, and also (3) the relative proportion of the sewage sludge constituents, such as the extractives content or the moisture content. Furthermore, the wastewater purification treatments and the stabilization and conditioning treatments are not standardized in wastewater treatment plants. For this reason, even when using the same treatments the composition of sewage sludge samples obtained from different urban wastewater treatment plants may vary significantly [46].

As with lignocellulosic biomass pyrolysis products [34], sewage sludge pyrolysis products come mainly from the individual pyrolysis of their constituents [47]. However, the simultaneous pyrolysis of all these constituents may have a synergetic effect on the pyrolysis products obtained from the reaction. This synergetic effect is related with the secondary reactions of the primary pyrolysis products obtained from the different sewage sludge constituents. For example, the primary pyrolysis products obtained from cellulose and compounds with amino groups could produce aminoacids [48].

As can be observed in Table 2, sewage sludge samples from different treatments have been used in pyrolysis studies for liquid production. Anaerobically digested and thermally dried sewage sludge samples are the most commonly used in these studies, although wet sewage sludge or non-stabilized samples have also been utilized. The reason that the anaerobically digested and thermally dried sewage sludge is the most extensively used in the pyrolysis investigations is probably that this kind of sewage sludge is produced in high capacity urban wastewater treatment plants. Table 2 also shows that some sewage sludge samples were previously washed with acid in order to eliminate ash.

As mentioned above, in most studies the sewage sludge samples used were dried in order to reduce their moisture. In the following sections, it will be explained that in pyrolysis for liquid production, the moisture of the raw material ends up in the liquid product unless a selective condensation system is used [63–65]. Usually, it is attempted to avoid high water contents in the liquids in order to use them as fuels. Furthermore, the dry sewage sludge obtained in wastewater treatment plants has a granulometric shape (see Fig. 2) and is easily smashed. This favors its feed and processing in conventional chemical reactors such as fluidized beds. Lastly, in general dry sewage sludge has good fluid-dynamic characteristics and can be classified as a solid type B according to the Geldart classification [66]. In fact, some pyrolysis experiments have been carried out in a fluidized bed with a mixture of sand and pyrolysis char [49] or even without the utilization of any coadjutant solid and using only the char obtained in the reaction as bed material [67].

Table 2
Characteristics of sewage sludge samples used in some investigations into the pyrolysis of this material.

Reference	Sewage sludge (SS) used
Piskorz et al. [49]	Digested and dry raw SS Digested and dry acid washed SS
Kaminsky et al. [50]	Digested and dry SS
Stammbach et al. [51]	Anaerobically digested and dry SS from mechanical-biological treatment
Inguanzo et al. [27]	Anaerobically digested SS
Shen and Zhang [52]	Activated and dry SS
Dominguez et al. [53–55]	Aerobically digested SS
Karayildirim et al. [56]	Chemical and activated sludge, and primary sludge
Park et al. [57]	Digested and dry SS
Kim and Parker [33]	Anaerobically digested and dry SS treated with acids and bases before the pyrolysis
Fonts et al. [58–60]	Anaerobically digested and dry SS
Pokorna et al. [61]	Two types of activated and dry SS. Digested and dry SS.
Sánchez et al. [62]	Anaerobically stabilized SS
Gil-Lalaguna et al. [63]	Anaerobically digested and dry SS

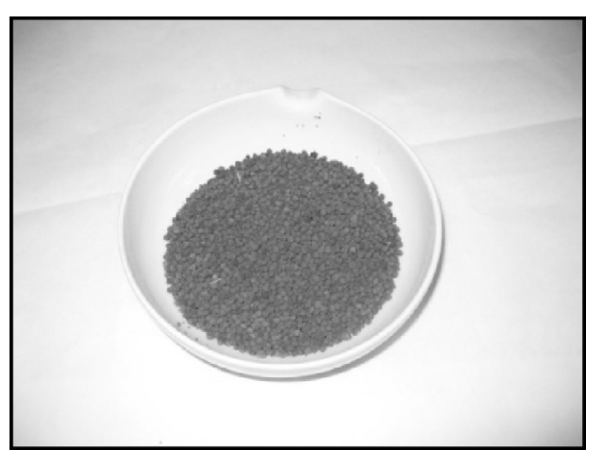


Fig. 2. Sewage sludge anaerobically digested and thermally dried as received from wastewater treatment plants.

Table 3
Composition of sewage sludge used in pyrolysis studies.

Ultimate analysis		Proximate analysis	
C (wt%)	23.1–39.9	Moisture (wt%)	1.5–7.1
H (wt%)	3.8–5.9	Ash (wt%)	22.6–52.0
N (wt%)	2.5–7.9	Volatiles (wt%)	38.3–66.8
S (wt%)	0.8–1.0	Fixed carbon (wt%)	0.8–19.7
O[a] (wt%)	18.8–23.5		

[a] Oxygen calculated by difference.

Due to the differences in their origin and treatments, the proximate and ultimate analyses of the sewage sludge samples used in these studies vary significantly (see Table 3). Not only is this due to the different types of sewage sludge, but also to the fact mentioned above that samples generated by the same treatments can vary significantly in their composition.

If sewage sludge ultimate analyses are compared with those relating to lignocellulosic biomasses, it can be appreciated that sewage sludge has considerably higher nitrogen content. The nitrogen in sewage sludge comes mainly from the protein fraction of this material, which has its origin in the microorganisms used for water purification. This high nitrogen content could favor the utilization of some fraction of the pyrolysis liquid as a fertilizer [36,68], although it could make its use as a fuel difficult. The proximate analyses reveal the high ash content compared to lignocellulosic materials. This fact causes for example that the reactors used to continuously process sewage sludge should be equipped with a continuous ash removal system.

The ash from sewage sludge contains mainly minerals such as quartz, calcite or microline. These minerals are formed by elements such as Fe, Ca, K and Mg that can catalyze some pyrolysis reactions. Furthermore, some heavy metals can also be found in the sludge (Cr, Ni, Cu, Zn, Pb, Cd, Hg) [46].

Some authors have shown other aspects of the chemical composition of sewage sludge such as its FTIR spectrum or the amount and composition of the extractives present in the samples. The FTIR spectra of various digested sewage sludge samples show the same functional groups, although with slight differences in the proportion of these groups [46,55,69]. The extractive content is quite high (around 7 wt% dry ash free) in comparison with other biomasses [46,70]. These extractives consist mainly of fatty acids, aliphatic hydrocarbons and steroids. As will be discussed in the following sections, the extractives have an important effect on the liquid properties and especially on the phase separation of pyrolysis liquids, as well as the heating value and the viscosity [44].

The heating value of the sewage sludge is affected by the type of sample and is greater when the moisture content and the ash content are lower, but also when the organic matter has not been digested. For this reason the higher heating value of digested and dry sewage sludge may range between 8.5 and 17 MJ kg^{-1} and, when the sample has not been digested, it can reach a considerably higher value (23 MJ kg^{-1}). The origin of the sewage sludge may also have an important effect on its heating value. Sludge obtained in the purification of wastewater from certain industries such as canned food or petrochemicals has significantly higher heating values than that obtained from urban wastewater treatment plants.

Lastly, in order to understand the pyrolysis of sewage sludge, the chemical composition of the material (organic and inorganic constituents and their relative proportions) must be taken into account. As regards the organic constituents, the main issue to be considered is the products that can be obtained from their pyrolysis. On the other hand, some elements present in the inorganic constituents of the sewage sludge may have a catalytic effect on the pyrolysis, as highlighted by some authors who have studied the pyrolysis of both sewage sludge and of lignocellulosic materials [46,49,71–75].

Table 4
Operational conditions of some sewage sludge pyrolysis experiments performed in fluidized bed systems.

Reference	Feed material	SS particle size (μm)	T (°C)	Solid feed rate (kg/h)	Gas flow rate (Ndm^3/min)	Solid residence time (min)	Gas residence time (s)	u/u_{mf}	Fluidizing medium
Piskorz et al. [49]	Digested dry raw SS	−250 (lab-scale)	400	5×10^{-3}–0.1			0.3		N_2, H_2 and CH_4
	Digested dry acid washed SS	−595 + 250 (pilot scale)	−700				−1		
Kaminsky et al. [50]	Digested dry SS	−1500 + 500	620–750	25–40					Pyrolysis product gas
Stammbach et al. [51]	Anaerobically stabilized SS from mechanical–biological treatment	−2000 + 100	485–645	1–5				1–30	N_2
Shen and Zhang [52]	Activate SS	−355 + 212	300–600	0.2–0.24			1.5–3.5	5	N_2
Park et al. [57]	Digested dry SS	−1400 + 800	446–720	0.3–0.66	25–31.7		0.2–0.5		N_2
Fonts et al. [58,60,91]	Anaerobically digested and dry SS	−500 + 250	450–650	0.18–0.36	3.5–5.5	3–8	1–3	6–15	N_2
Park et al. [89]	Dried SS	−1000 + 300	400–550	0.102–0.3	3–5				N_2 and pyrolysis product gas

u: gas velocity; u_{mf}: minimum fluidization velocity.

Furthermore, the relative proportion of sewage sludge constituents such as extractives and moisture may strongly affect the characteristics of the liquids obtained from pyrolysis [44,46,76,77]. All these important effects of the sewage sludge composition on the pyrolysis process are explained in depth in the following sections.

3. Types of studies about sewage sludge pyrolysis

Numerous authors from the 1980s have investigated the pyrolysis of sewage sludge with different objectives. According to these objectives, the studies can be classified into the five following groups: thermogravimetric studies of sewage sludge pyrolysis focused on the reaction kinetics and also on the composition of the non-condensable gases obtained, analytical pyrolysis studies centered on the characterization of the sewage sludge composition, sewage sludge pyrolysis for the production of solid adsorbents, sewage sludge pyrolysis for obtaining a syn-gas and, finally, sewage sludge pyrolysis for liquid production. Some of the main works found in each of these groups are discussed below.

3.1. Thermogravimetric pyrolysis studies

Thermogravimetric studies of sewage sludge pyrolysis have been carried out by some authors with the main objectives of finding out the kinetics of the reaction and also of knowing the composition of the non-condensable gases. In this way, Urban and Antal [78] investigated the thermal decomposition of four samples of sewage sludge and developed a model consisting of two parallel competitive reactions in which a solid and a gas product were obtained. The kinetics of sewage sludge pyrolysis has also been studied proposing a kinetic mechanism from thermogravimetric data involving primarily various parallel competitive reactions [79,80]. Other authors have studied the composition of the non-condensable gases obtained from thermogravimetric experiments of sewage sludge pyrolysis by gas chromatography–mass-spectrometry (GC–MS) [28,29]. In both works, it was found that the weight loss occurs principally in three stages, centered around 250, 350 and 550 °C, producing high quantities of gases such as H_2, water, hydrocarbons (C1 ± C4, both saturated and unsaturated), methanol, carbon dioxide and acetic acid. Furthermore, Caballero et al. [28] and Urban and Antal [78] performed differential scanning thermogravimetric analyses that enabled them to indicate approximately the amount of enthalpy necessary to pyrolyze certain sewage sludge samples at temperatures between 200 and 800 °C. For example, they reported that the reaction energy needed for sewage sludge pyrolysis at 500 °C was around 300 J/g. This information was used by Kim and Parker [33] in order to evaluate energetically the pyrolysis of sewage sludge for liquid production. Lastly, Ischia et al. [81] used clay in a TG-MS study to evaluate the possible advantages of co-pyrolysis of clay and sewage sludge. Two main effects were observed. Firstly, the clay surface catalyzed the pyrolysis reaction of the sludge and, secondly, the release of water from the clay, at temperatures of 450–500 °C, enhanced the gasification of part of the carbon residue of the organic component of the sludge.

3.2. Analytical pyrolysis

Parnaudeau and Dignac [47] analyzed the composition of urban and industrial sewage sludge samples by means of analytical pyrolysis and gas chromatography–mass spectrometry. They found that the pyrolysis of all of the sewage sludge samples yielded to compounds derived from polysaccharides, lipids and also from the protein fraction of the sludge. However, lignin-derived products were, in contrast, only present in the pyrolysis products of two sludge samples, and were especially abundant in the sludge composted with green wastes and wood pieces.

3.3. Pyrolysis for the production of solid adsorbents

Sewage sludge pyrolysis has also been investigated with the aim of obtaining a solid product that can be used as adsorbent [82–85]. The specific surface area of char obtained from the pyrolysis of sewage sludge, once activated, can reach values around 360 $m^2\,g^{-1}$, whereas the commercial activated carbons show values significantly higher (500–1200 $m^2\,g^{-1}$). However, according to numerous authors, the adsorbents obtained from sewage sludge pyrolysis chars may play an important role in the elimination of contaminants such as H_2S and NO_x generated in thermochemical processes [86–88]. Furthermore, they can also be used to eliminate metals, dyes and phenols [32].

3.4. Pyrolysis for obtaining a syn-gas

Other studies about sewage sludge pyrolysis have focused on the production of a syn-gas. These experiments have been performed at high temperatures (1000 °C), in electric and microwave ovens and, occasionally, using sewage sludge samples with a high moisture content [54,55]. When sewage sludge with high water contents is thermally treated, this process may be considered as a gasification process in which the gasification agent is water. In these investigations, a maximum value of 38 vol% for H_2 and 66 vol% for H_2 + CO were obtained due to the displacement of the water gas shift reaction. In general, sewage sludge samples with a high moisture level would be beneficial for the production of gas, because this would favor hydrogen production by the displacement of the water gas shift reaction.

3.5. Pyrolysis for liquid production

The last group of investigations found in the literature is related to the pyrolysis of sewage sludge for liquid production. The state of the art of this kind of study is reviewed in this publication and will be discussed in depth in the following sections.

4. State of the art of sewage sludge pyrolysis for liquid production

Several researchers have focused their studies on liquid production from sewage sludge pyrolysis as a promising alternative for its management. This section seeks to review the literature concerned with liquid production from sewage sludge pyrolysis, and in particular the reactors and operational conditions used, the liquid yield obtained and the effect of the operational conditions on that yield, on the liquid physicochemical properties and on the liquid chemical composition. Finally, the possible applications of sewage sludge pyrolysis liquids will be discussed, paying special attention to the information published about Enersludge Technology, which built a field-scale sewage sludge pyrolysis plant for liquid production in Perth (Australia).

4.1. Operational conditions in sewage sludge pyrolysis for liquid production

The studies about sewage sludge pyrolysis for liquid production can be divided into two groups: those in which no catalyst is used, which are significantly more abundant, and those in which a catalyst is used. Next, the main characteristics of the operational conditions utilized in these studies will be described.

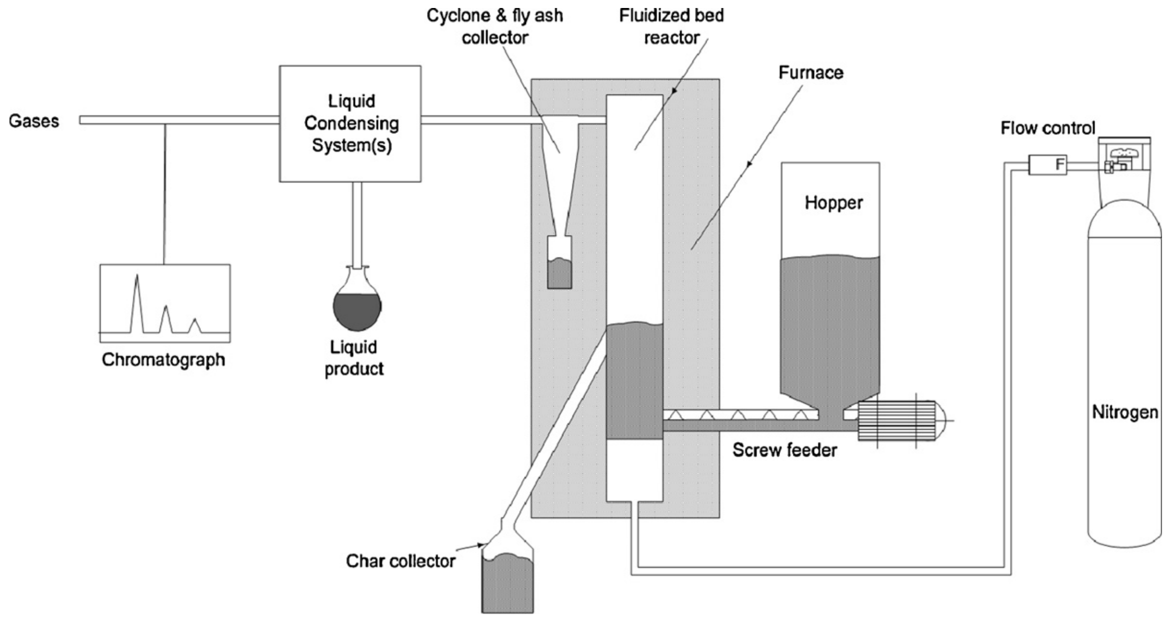


Fig. 3. Typical schematic of fluidized bed systems used in sewage sludge pyrolysis experiments.

4.1.1. *Non-catalytic pyrolysis*

Since the liquid is the pyrolysis product of interest, most of the research works have been performed using fluidized bed reactors in order to achieve the essential features of a fast pyrolysis process [49–52,57,58,89]. In general, the fluidized bed system used by different authors is similar. The experimental apparatus are bench scale plants equipped with a fluidized bed reactor operating at atmospheric pressure. The sewage sludge is fed from a hopper by a screw feeder above the distribution plate of the reactor. Sand is added as inert material in the bed, although some authors did not use a coadjutant solid for the fluidization [67]. Nitrogen is used as fluidizing gas, although sometimes the non-condensable gases from the pyrolysis itself are recirculated and used as fluidizing agents [50,57]. The product gas leaves the reactor and goes through a cyclone where most fine solid particulates are collected. The product gas is then cooled in a condenser train where the pyrolysis liquid is collected and the non-condensable gases are analyzed by gas chromatography. Most of the condensation systems are formed by cold traps in series followed by a column pack with cotton [49,58] or followed by an electrostatic precipitator [46,50,51]. The temperature cooling media used in the condensers varies from −30 °C [51,57] to 0 °C [49,50,58]. Shen and Zhang [52] used a shelf and tube stainless steel condenser with water as cooling media. Gil-Lalaguna et al. [63] substituted the cold traps by a scrubber with different polar cooling liquids followed by an electrostatic precipitator. The aim of using this liquid recovery system was to reduce the water content of the liquids condensing selectively in the scrubber or in a subsequent electrostatic precipitator the vapors produced in the reaction. Lastly, Cao et al. [90] designed a reactive condensation system in which the pyrolysis vapors were collected in a scrubber using acetone, with the aim of producing triacetonamine. A typical diagram of the fluidized bed systems used for sewage sludge pyrolysis is depicted in Fig. 3.

Table 4 shows some of the operational conditions used in fluidized bed systems.

Some sewage sludge pyrolysis experiments have also been performed in fixed bed reactors [27,33,53–55,92]. The typical fixed bed reactor system for sewage sludge pyrolysis is a horizontal quartz [27,53,92] or stainless steel reactor [33] heated by either electrical [27,33,92] or microwave furnaces [53–55]. The sample of sewage sludge is placed inside the reactor and heated at a controlled heating rate from room temperature to a final pyrolysis temperature in an inert atmosphere. The volatiles derived from the sample go through ice/water cooled condensers and, sometimes, through ice cooled U tubes with Rasching rings [92] where the liquid is collected. The non-condensable gases are also analyzed by GC [27]. Table 5 shows some of the operational conditions used in the fixed bed reactor systems.

Some authors have researched sewage sludge pyrolysis using less conventional reactors. For example, Pokorna et al. [61] used a semi continuous vertical reactor. Within the reactor, sand, in constant motion by means of an Archimedes' screw, was used as a heat transfer medium. Sewage sludge was directly injected into the reactor by another Archimedes' screw at a feed rate of 200 g of sludge in 90 s. A flow of 140 mL/min of N_2 was used to guarantee an oxygen deficient atmosphere. The pyrolysis temperature analyzed was 500 °C. The liquid recuperation system consisted of water cooled equipment and a collector vessel at room temperature.

Considering the most relevant reactor designs used for fast pyrolysis of lignocellulosic biomass [93], to the best of the authors' knowledge, the ablative plate pyrolysis reactor, the rotating cone reactor, vortex reactors and vacuum pyrolysis reactors have not been tested with sewage sludge to date.

4.1.2. *Catalytic pyrolysis*

Research in catalytic pyrolysis of sewage sludge is very limited, and much of it is based on previous work using lignocellulosic materials and lipids as feedstock, given the similarity of the composition of these two materials with that of sewage sludge [94–98]. The catalysts used in the investigations into the catalytic pyrolysis of lignocellulosic biomass are mainly zeolites, while the catalytic pyrolysis of lipids and triglycerides is based on the use of gamma-alumina. Both types of catalytic studies are focused on the reduction of the oxygen content of the liquids in order to improve the hydrogen to carbon ratio and in consequence properties such as the heating value or stability. For instance, there are several studies focused on the in-bed use of zeolites to improve the energetic density of the product, increasing the hydrogen/carbon ratio. Together with these effects, the use of these catalysts may imply a change in the product distribution, above all the liquid and the gas yield and a change in the liquid and gas characteristics.

Table 5
Operational conditions of some sewage sludge pyrolysis experiments performed in fixed bed systems.

Reference	Feed material	SS particle size (mm)	Sample mass (g)	Temperature (°C)	Inert gas flow rate (mL/min)	Heating rate (°C/min)
Inguanzo et al. [27]	Anaerobically digested SS	1–3	20	450–850	100 (N_2)	5–60
Dominguez et al. [53–55]	Aerobic digested SS			800–1200	10–15 (He)	74–300
Karayildirim et al. [56]	Chemical and activated sludge, and primary sludge	1	140	500	25 (N_2)	7
Kim et al. [33]	Anaerobically digested SS		5	250–500	50 (N_2)	
Sanchez et al. [92]	Anaerobically stabilized SS	2–3	30	350–950	100 (He)	30

As regards the catalytic pyrolysis of sewage sludge, there are still few studies about the effect of the use of catalyst in the process [33,51,76,81,89,99–101]. Many of these studies also aim to reduce the oxygen content of the liquid product in order to improve its properties such as heating value or viscosity. Moreover, there are also some studies focused on the reduction of the pyrolysis temperature or on the reduction of the chlorine content of the liquid. However, to the best knowledge of the authors, the catalytic pyrolysis of sewage sludge has not yet been directed at a reduction of the nitrogen content of the liquid.

Apart from sewage sludge itself, the lipids extracted from it have also been used as feed material. Catalytic conversion using activated alumina of triglycerides and fatty acids has been studied because of the fact that sewage sludge contains considerable amounts of fatty acids. Some authors have shown different conversion pathways of triglyceride decomposition to obtain aliphatic compounds such as alkanes and alkenes using activated alumina as catalyst [97,98]. Summarising, when the fed material is sewage sludge, different catalysts such as γ-alumina, zeolites, clay, $CuSO_4$, Fe_2O_3 or cement have been used (see Table 6). Table 6 summarizes the main characteristics of the studies about the production of pyrolysis liquids from sewage sludge using a catalyst in the pyrolysis system. These characteristics are material fed, pyrolysis temperature, kind of catalyst, type of catalytic pyrolysis reactor and main aim of the study.

4.2. Liquid yield: influence of various parameters

The pyrolysis liquid from sewage sludge mainly consists of water and organic compounds. Some authors count the liquid yield as including both water and organic compounds [27,33,46,52,58,102], but others quantify water and organics yields separately, or aqueous and organic phase yields [49–51,57].

The maximum liquid yields from sewage sludge pyrolysis are in the range of approximately 27–54 wt% on sewage sludge fed basis or 51–80 wt% on dry ash free (daf) basis. Shen and Zhang [52] reported an especially low value of liquid yield around 30 wt% daf compared to liquid yields obtained from wood and other lignocelullosic biomasses, which are approximately 60–75 wt% [34]. Although the liquid yield from sewage sludge may seem to be much inferior, the much lower ash content of biomass should be taken into account in this comparison. For this reason the liquid yield from sewage sludge expressed on dry ash free basis is more comparable to bio-oil yields from lignocellulosic biomass.

Table 7 shows the maximum liquid yield reported by several authors with the corresponding moisture and ash content of the sewage sludge fed. In Table 7, the data for oil and water yields are also indicated for those references whose authors express them separately. As can be observed, the water yield is always higher than the moisture content of the initial sewage sledge sample which means that water is produced during decomposition and/or secondary reactions of sewage sludge primary pyrolysis products. According to Karayildirim et al. [56], at over 200 °C the water product comes from dehydration reactions and from the degradation of oxygen-containing high molecular compounds.

The broad interval for the maximum liquid yield value (51–80 wt% daf) is due to the great influence of the sewage sledge composition and the operational conditions on the liquid yield. The operational conditions at which the maximum yield is obtained are also shown in Table 7 for each reference. Lastly, the values shown in Table 7 correspond to the maximum yields of the whole liquid, although there may be other operational conditions that maximize the yield of the organic phase. All the sewage sludge samples used by these authors were anaerobically digested and thermally dried, except that used by Pokorna et al. [61] which was non-digested but thermally dried.

Several papers are focused on analyzing the influence of sewage sludge composition and operational conditions on the pyrolysis product yields, specifically the liquid yield, with the objective of optimizing the liquid production. The process variables whose effect on the liquid yield has been analyzed are the following: (a) temperature, (b) gas residence time, (c) solid feed rate, (d) sewage sludge particle size, (e) reaction atmosphere composition, (f) sewage sludge composition, (g) use of catalyst.

4.2.1. Influence of temperature

The effect of the pyrolysis temperature on the liquid yield is probably the most studied one. The temperature intervals used by several authors to analyze this influence are shown in Tables 4–6. The temperature at which the maximum liquid is obtained by the various authors is indicated in Table 7.

Most of the sewage sludge pyrolysis works performed in fluidized bed plants show an increase in the liquid yield with the bed temperature until reaching a maximum yield over the temperature range of 450–550 °C [49,51,52,58,89]. Initially, the liquid yield increases with increasing temperature because the temperature promotes the devolatilization of organic matter. This is because there is more energy available to break the strong organic bonds. The decrease in the liquid yields above the optimal temperature is believed to be a result of secondary reactions of the volatiles such as thermal cracking, which are known to become significant at temperatures higher than approximately 500 or 550 °C. This behavior is also typical of biomass pyrolysis in fluidized beds [43].

The disparity found between authors about the optimal temperature for maximizing the liquid yield could be due not only to the influence of the sewage sludge composition but also to the interactions between the temperature and other operational variables [51,57,58,89].

In the case of sewage sludge pyrolysis experiments carried out in fixed bed reactors, the liquid yield increases as the temperature increases since the liquid product is the result of the

Table 6
Summary of the studies about catalytic pyrolysis of sewage sludge.

Reference	Fed material	Temperature (°C)	Catalyst	Catalytic pyrolysis reactor	Aim
Konar et al. [101]	Lipids extracted from dried SS	450	γ-Al_2O_3	Fixed bed	Liquid to be used as diesel fuel.
Bahadur et al. [76]	Lipids extracted from dried SS	450	γ-Al_2O_3	Fixed bed	Evaluation of liquid properties produced by the catalytic pyrolysis of lipids.
Beckers et al. [99]	Digested dry SS	600	Y-Zeolite	Fluidized bed + FCC	Effect of the catalytic treatment on the product distribution obtained from the pyrolysis of sewage sludge.
Stambach et al. [51]	Anaerobically digested and dry SS	450–650	FCC Zeolite	Fluidized bed	To improve the yield to high quality liquid products by means of the use of a fluid-cracking catalyst.
Guang et al. [100]	Digested dry SS	300-600	$CuSO_4$, Fe_2O_3, cement, ash	Rotatory oven	To decrease the pyrolysis temperature with additives such as cement, bluestone, ash of sludge and ferric oxide. Effect on the product distribution.
Kim and Parker [33]	Digested dry SS	250–500	Zeolite	Fixed bed	Techno-economic evaluation of the catalytic pyrolysis of SS.
Park et al. [89]	Digested dry raw SS	400–550	CaO La_2O_3 CaO/Al_2O_3 La_2O_3/Al_2O_3	Fluidize bed + fixed bed	To reduce the chlorine content of bio-oil by means of catalytic pyrolysis.
Ischia et al. [81]	Dry SS	450–500	Clay	TG	To study the possible benefits that clay entails in sewage sludge pyrolysis.

accumulation of the condensable vapors produced in each temperature stage studied [27,33,102].

The influence of the temperature on the water and on the organic fraction yield has been analyzed separately by some authors [49,51]. The organic fraction shows a maximum yield over the temperature range 400–550 °C. In the case of the water yield, Piskorz et al. [49] observed a maximum yield at 550 °C, although the water yield is less influenced by temperature than the organic fraction yield. However, Stammbach et al. [51] detected a water yield decrease with increasing temperature in the same temperature interval as that analyzed by Piskorz et al. [49]. Water is probably formed from the decomposition of sugars and acids below 500 °C [51], and also from condensation reactions [49]. On the other hand, it may be expected that the water yield would increase when the temperature increases, because water is involved in the water gas shift reaction, the most important gas phase reaction in the thermodynamic processes. This reaction occurs very quickly (kinetic) and the formation of water (reactive of the water gas shift reaction) is favored, since this reaction is slightly exothermic [51].

Finally, several authors coincide in identifying the temperature as the most influential operational variable on the liquid yield [51,58,89]. For this reason, in order to maximize the liquid yield it is indispensable to find the optimum temperature.

4.2.2. *Influence of gas residence time*

According to biomass pyrolysis studies, a gas residence time lower than two seconds is required in order to obtain a high liquid yield. It is claimed that the lower the gas residence time, the higher the liquid yield because the thermal cracking reactions have less time in which to take place. Unlike the effect of the gas residence time on the biomass pyrolysis liquid yield, its effect on the sewage sludge liquid yield observed by different authors is not totally coincident. This effect has been studied by several authors by modifying the inlet fluidizing gas flow [57,58,89], so the effect of the fluidization regime should also be taken into account. Furthermore, the variation in the nitrogen flow rate would vary the degree of dilution of the pyrolysis vapors. When the dilution of the vapors increases, the pressure decreases and this makes it more difficult to reach saturation pressure. This affects the condensation and thus the liquid yield.

Piskorz et al. [49] and Fonts et al. [58] detected a maximum liquid yield within their intervals of study, whereas Shen and Zhang [52] and Park et al. [89] viewed a continuous liquid yield decrease with increasing gas residence time. Piskorz et al. [49] also detected a maximum yield to organics at the shortest gas residence time, but since the water yield increased with the gas residence time the total liquid yield showed a maximum value in the range of gas residence time studied.

Several reasons could explain the variability reported by the different authors. Firstly, the interval used to analyze the effect of the gas residence time differs among the works. These intervals are shown in Table 4. Secondly, most authors studied the gas residence time at one pyrolysis temperature only, at 450 °C [49,57] or 525 °C [52]. However, some authors [58] found out that the effect of the gas residence time on the liquid yield could depend on the pyrolysis temperature used.

In spite of the discrepancies between authors about the effect of the gas residence time, they all coincide in explaining the decrease in the liquid or the organic fraction yield with increasing gas residence time by the occurrence of secondary cracking reactions which transform larger species of the vapors into non-condensable gases.

The increase in the liquid yield with the gas residence time could have several explanations. Piskorz et al. [49] assume that the increase in the water yield provokes an increase in the liquid yield at gas residence times between 0.3 and 0.55 s. The water yield increases due to possible condensation reactions with water as a byproduct. These reactions could be favored by long gas residence times [49]. On the other hand, since the gas residence time is inversely proportional to the gas flow rate and therefore to the ratio between the fluidization velocity and the minimum fluidization velocity (u_f/u_{mf}), Fonts et al. [58] indicate that very low gas residence times (high u_f/u_{mf}) could cause some solid particles to reach their terminal velocity being elutriated from the bed without reaching their total conversion at the temperature studied. In this case, an increase in the gas residence time or decrement of the gas flow rate could prevent solid particles from leaving the bed without reaction and, therefore, could raise the liquid yield.

Table 7
Maximum liquid yields, sewage sludge characteristics (moisture and ash content), and operational conditions used to obtain these maximum yields reported.

Reference	SS moisture content (wt%)	SS ash content (wt%)	Liquid yield (wt% as SS fed basis)	Liquid yield (wt% daf)	Operational conditions
Piskorz et al. [49]	6.23	42.48	39.96 Oil 28.32 Water 11.64	67.87 Oil 52.65 Water 15.22	450 °C gas residence time: 0.55 s
Kaminsky et al. [50]	5.8	42.9	30.1 Organic phase[a] 20.5 Aqueous phase[a] 12.3	52.7 Organic phase 40.1 Aqueous phase 12.6	620 °C
Stammbach et al. [51]	5.1	40.7	43.04 Oil 16.26 Water 26.78	70.0 Oil 30.0 Water 40.0	500 °C
Inguanzo et al. [27]	5.0	29.6	40.0 (with 30–40% of aqueous phase)	61.2	650 °C heating rate: 60 °C/min
Shen and Zhang [52]	3	22.6	20.1	30.0	525 °C gas residence time: 1.5 s
Jindarom et al. [102]	6	46	30 (presence of an aqueous and an organic phase)	62.5	550 °C CO_2 atmosphere
Kim et al. [33]	0	n.r.	42 (primary sludge) (presence of an aqueous and an organic phase)	n.r.	500 °C
Park et al. [57]	5.56	26.81	54 Organic phase 28–31 Aqueous phase −23 to 26	72 Organic phase 37–41 Aqueous phase 31–35	450 °C solid feed rate: 0.66 kg/h SS particle size: <830 μm
Fonts et al. [58]	7.1	41	40.7 Oil 24.2 Water 16.5	64.7 Oil 46.6 Water 18.1	550 °C gas residence time: 2 s solid feed rate: 0.18 kg/h
Pokorna et al. [61]	1.5	25	43.1 n.r.	56.6 Aqueous phase 10.3 (vol%)	500 °C
Sanchez et al. [92]	6.8	32.4	31.0 Oil 13.0 Water 18.0	51.0 Organic phase 21.4 Aqueous phase 18.4	450 °C
Park et al. [89]	5.1	26.9	50.4	66.8 (liquid with water contents between 27 and 54%)	450 °C Gas flow rate: 5 L/min SS particle size: 0.7 mm Solid feed rate: 0.3 kg/h

n.r.: not reported.
[a] Calculated assuming that all the moisture remains in the aqueous phase.

4.2.3. *Influence of solid feed rate*

The solid feed rate could have several effects on the pyrolysis process and consequently on the liquid yield. It could affect the solid residence time in the reaction zone, the catalytic effect of the sewage sludge ash, and also the gas residence time, generating different effects on the liquid yield. A higher feed rate may imply lower solid residence time in the reaction zone (if the char is continuously removed by overflow), higher catalytic effect of the ash (since the sewage sludge ash has less time to lose its catalytic activity) and lower gas residence times (since the amount of gases generated in the reaction greatly increases).

Stammbach et al. [51] and Fonts et al. [58] observed that higher feed rates resulted in lower liquid yield. Stambach et al. [51] account for this trend by the reduction in the char conversion and therefore the decrease in the production of vapors and gases in the reaction. Moreover, Fonts et al. [58] claim also that the higher catalytic activity produced at higher solid feed rates could cause a decrease in the liquid yield due to the cracking of the organic condensable vapors.

However, Park et al. [57,89] obtained a higher liquid yield at a higher feed rate. A higher feed rate could also imply an enhancement in the gas flow and a reduction in the gas residence time. As mentioned above, lower gas residence times could prevent secondary cracking reactions and then provoke an increment in the liquid yield.

The effect of the solid feed rate on the liquid yield, therefore, seems to depend on the feed rate interval analyzed and on the value of the other operational variables.

4.2.4. *Influence of sewage sludge particle size*

The particle size also influences the liquid yield inasmuch as the reaction time for sewage sludge strongly depends on the particle size. Smaller particles heat up faster reaching a higher average temperature and requiring less time to devolatilize. Consequently,

smaller particles enhance the liquid yield [51,57,89]. This trend is consistent with previous studies carried out with lignocellulosic biomass [35,43]. However, Park et al. [89] also observed that too small particle size (<0.3 mm) could result in an overheating of the particle followed by conversion of the vapors into gas. Due to this fact, Park et al. [57,89] detected a maximum liquid yield for sludge particles of about 0.7 mm. Besides, the particle size distribution needs to be carefully chosen to avoid prior elutriation of the sludge and secondly a conversion drop [51].

4.2.5. Influence of reaction atmosphere composition

Recycling the gas product stream to provide a relatively oxygen-free atmosphere seems to be an economical way to operate a commercial-scale pyrolysis plant [102]. For this reason some authors have evaluated the effect of the reaction atmosphere composition on the liquid yield. Pyrolysis experiments have been carried out in methane, hydrogen and carbon dioxide atmospheres as well as nitrogen atmospheres. Piskorz et al. [49] compared hydrogen and methane atmospheres with nitrogen atmosphere at 500 and 650 °C, observing the higher liquid yields with the hydrogen atmosphere at the lower temperature. However, at the higher temperature, the hydrogen and methane presence reduced the liquid yield and increased the light hydrocarbon gas yields. Jindarom et al. [102] compared carbon dioxide with nitrogen atmosphere over the temperature range of 350–650 °C detecting an increase in the liquid yield in the presence of CO_2 because CO_2 seems to facilitate the formation reactions of gas and liquid products [102]. This trend is probably due to CO_2 being more reactive than N_2.

Other authors have carried out sewage sludge pyrolysis using the gas product stream as the fluidizing medium [50,57,89]. According to their results, the product gas, consisting mainly of CO, CO_2 and H_2, may affect the pyrolysis or vapor phase reactions, increasing the liquid yield, at least at the temperature studied (450 °C) [89].

4.2.6. Influence of sewage sludge composition

Urban wastewater purification treatment is a complex process with numerous steps, and the composition of the sludge collected in the different steps is different. In general, three types of sludge may be distinguished: primary sludge, secondary or activated sludge and digested sludge. Some authors have compared the liquid yield obtained from the pyrolysis of sludge collected in the different steps [33,56,61]. Primary sludge produced higher liquid yields than secondary sludge which in turn produces higher yields than digested sludge because of the higher volatile contents. This is because the pyrolysis liquid is expected to come from the devolatilization of the volatile materials [103]. Besides, the liquid yields normalized on a volatile basis from the primary and secondary sludges are similar, but higher than the liquid yield obtained from digested sludge [33], which may indicate that primary and secondary sludge contain more liquid precursors which are destroyed during the sludge digestion process [104]. Therefore, primary sludge seems to be more suitable than secondary or digested sludge for enhancing the liquid yield in pyrolysis. Furthermore, Kim and Parker [33] claim that the temperature has a different effect depending on the kind of sewage sludge. According to them, the oil yields of primary and digested sludge increase more steeply over the temperature range between 250 and 350 °C, while TWAS (thickened waste activated sludge) increases steadily up to 450 °C.

On the other hand, as commented in Section 2, even sludge samples collected from the same process step and coming from the same wastewater purification and sludge stabilization treatments can have different compositions due to the wastewater origin and the non-standardized treatments applied in wastewater treatment plants. Fonts et al. [46] analyzed the influence of some aspects of digested sludge composition on the pyrolysis process. The organic and inorganic material of three anaerobically digested sludge samples were characterized by means of proximate and ultimate analysis, soxhlet extraction, FTIR analysis, inductively coupled plasma-optical emission spectroscopy (ICP-OES), atomic absorption spectroscopy (AAS) and X-ray diffraction. This characterization evidenced significant differences in the ash and volatile contents, and in the organic and inorganic matter composition. These differences affected the pyrolysis product yields. The results of this study indicated that sewage sludge samples with low ash contents and high volatile contents seem to be appropriate in order to enhance liquid production. Piskorz et al. [49] also found that the use of char instead of sand as inert fluidized material decreased the liquid yield. This fact is due to the presence of sodium and calcium in the sludge ashes concentrated in the char, which are known gasification and cracking catalysts. These trends are consistent with some studies of lignocellulosic biomass pyrolysis [44,72,105]. The presence of alkaline cations in biomass affects the mechanism of decomposition reactions in the pyrolysis [34]. The presence of potassium, lithium and calcium cations seems to reduce liquid yields [106]. In the same way, Oasmaa et al. [105] showed that the decrease in the liquid yield obtained from different lignocellulosic biomasses can be correlated with the increase in their contents of alkali metals or (Na + K).

In the liquid, both the organic and the water yields are influenced by the sludge composition. The water yield seems to augment with the quantity of OH groups in the raw sewage sludge composition [46,56]. Indeed, some authors have indicated that pyrolysis water could be produced in secondary pyrolysis dehydration reactions of primary pyrolysis products which contain oxygen [56,107].

Fonts et al. [46] proposed as a worthwhile subject of further investigation whether a higher ash content in the sludge could reduce the optimal temperature required for maximizing the liquid yield. Higher ash contents may favor the contact between the metal of the ash and the organic matter and would cause the devolatilization reactions to take place at lower temperature regions.

4.2.7. Influence of the catalytic pyrolysis

Although very limited in number, catalytic pyrolysis studies indicate a decrease in the yield to the whole liquid product when a catalyst is used in the pyrolysis system (see Table 8). Such decreases may be caused by an increase in the catalytic cracking reactions.

4.3. Physico-chemical properties of liquid

The liquid from sewage sludge pyrolysis is a dark brown organic fluid with a high water content. The evaluation of pyrolysis for liquid production as a means of sewage sludge management requires knowing not only the liquid yield, but also the liquid characteristics in order to be able to propose appropriate liquid applications or recommending upgrading treatments, like the one proposed by Doshi et al. [108]. Most authors propose energetic applications for the pyrolysis liquid and for this reason the properties which are important for its use as a fuel have been the most extensively analyzed. Specifically, the liquid properties reported in the literature are the following: homogeneity, water content, heating value, solid content, viscosity, density, pH, ammonia content, elemental analysis and toxicity. On the other hand, the knowledge of the composition of the liquid is also important to determine its possible use as source of valuable chemical products and also enables a deeper understanding of the reactions occurring in the pyrolysis process.

The physicochemical properties determine the liquid quality, and the quality required depends on the application targeted. The interest in the quality of pyrolysis liquids is growing, and it is recognized that the operating conditions which maximize the liquid yield do not necessarily coincide with those which maximize the liquid quality [109]. Therefore, the optimization process should take into

Table 8
Summary of the influence of the catalytic pyrolysis on the liquid yield.

Reference	Temperature (°C)	Catalyst	Liquid yield without catalyst (wt%)	Liquid yield with catalyst (wt%)
Beckers et al. [99]	600	Y-Zeolite	Oil 40 Water 13	Oil 25 Water 21
Kim and Parker [33]	250–500	Zeolite		Decrease when the ratio catalyst/sewage sludge increases over 1.5
Park et al. [89]	400–550	CaO La_2O_3 CaO/Al_2O_3 La_2O_3/Al_2O_3	43	39

account simultaneously both the liquid yield and quality. For this reason it is important to know in depth the effect of the operational conditions not only on the liquid yield but also on the liquid properties and composition.

The liquid properties and composition provided by the authors who have studied the pyrolysis of sewage sludge are discussed below. Most of these authors have determined the physicochemical properties at certain specific operational conditions and only a few have evaluated the influence of operational variables on these properties.

4.3.1. Homogeneity

Many works about the production of pryrolysis liquid from sewage sludge have concentrated on the heterogeneity of the liquid. This heterogeneity leads to a phase-separated liquid. The phase separation of the liquid into an organic and an aqueous phase [27,31,50,57,60,61] or even into two different organic phases and an aqueous phase [60,63,67] has been highlighted by various authors. Some of these authors have only determined the phase separation in the liquid, while others have studied the effect of the operational conditions on it.

The literature review has shown that the proportion and properties of organic phase obtained in the different studies varies significantly. For instance, Inguanzo et al. [27] or Briddle and Pritchard [31] obtained a proportion of organic phase of around 60 or 70%, Park et al. [57] of between 52 and 57% and Pokorna et al. [61] of around 44%.

The phase separation of the liquid has been shown to be affected by the temperature [50,60], the kind of sewage sludge [60], the procedure used to study the phase separation (gravity or centrifugation) [67] and the operational conditions of the liquid condensation system [63]. Kaminsky and Kummer [50] found that the proportion of organic phase decreased from 76 to 72% when the temperature increased between 620 and 750 °C. In the study carried out by Fonts et al. [60], the temperature also had an effect on the phase separation affecting even the number of phases that appeared in the liquid. Furthermore, these authors also determined that the variation in the liquid composition, specifically in the liquid water content and the amount of extractives, produced by changes in the composition of the sewage sludge also has a strong effect on the phase separation. This fact is due to the important influence of the kind of sewage sludge on the liquid composition. Similarly, when the liquid composition changes, for instance the water content, the distribution of the phases is strongly affected [63].

According to Beckers et al. [99], the liquids obtained from non-catalytic and catalytic pyrolysis are heterogeneous and separate into two phases (see Table 8), although there are differences in the phase distribution with the water yield increasing with the catalytic treatment. The results of some catalytic pyrolysis experiments performed with activated gamma alumina by other Azuara et al. [110] seems to favor the separation of the compounds into two more distinctive phases, becoming the aqueous phase clearer in color. In these experiments, the two organic phases also combine in a single organic phase with a very high H/C ratio and, therefore very non-polar. The differences in the characteristics of these aqueous and organic phases, mainly in color and polarity, make their subsequent separation easier.

Taking into account the data found in the literature, this changeability of results appears to be caused by the differences in the operational conditions, the sewage sludge samples, the liquid condensation system, the procedure used to collect the liquid (pure or with solvent) or even the procedure used to analyze the phase separation (centrifugation or gravity).

4.3.2. Water content

Liquid water content comes from both the initial sewage sludge moisture and the water produced in the reaction. Karl Fisher titration is the typical analysis used to quantify the liquid water content, although some authors have used azeotropic distillation [61].

In general, water is the most abundant compound in pyrolysis liquid, and its quantification is of considerable interest because it influences enormously other important properties such as liquid homogeneity or liquid phase stability, low heating value and viscosity [111]. High liquid water content favors liquid instability with the presence of various phases, and decreases the low heating value and viscosity of the liquid.

The liquid from sewage sludge pyrolysis contains approximately between 20 and 70 wt% of water, depending on its composition and on the operational conditions. The wide water content interval reported is remarkable.

The temperature effect on liquid water content has been analyzed by several authors [49,60,92]. Some liquid water content values obtained from data reported by these authors are displayed in Table 9. In general, this data shows that liquid water content reaches a minimum value at temperatures between 400 and 550 °C. Fonts et al. [60] studied the temperature influence in the interval 450–650 °C. They observed a minimum water content of around 25 wt% at temperatures between 520 and 560 °C depending on the gas flow and feed rate values. Table 9 shows the data reported by Piskorz et al. [49], who also obtained a slight water content decrease between 350 and 400 °C and an increase between 400 and 700 °C. Sánchez et al. [92] studied the temperature effect in the interval 350–950 °C detecting a minimum water content of around 58 wt% at 450 °C (see Table 9). The variation of the water content with temperature depends on the variation of the water and total liquid yields. As already mentioned, the liquid yield shows a maximum over the temperature range of 450–550 °C. However, the water yield is nearly constant in the same interval [60,92] or shows a maximum but with much less variation with the temperature than the liquid (organic) [49]. For this reason, the water content seems to show a minimum in that temperature range. The temperature

Table 9
Water content of liquid obtained from sewage sludge pyrolysis at different temperatures.

Reference/most relevant operational conditions	Temperature (°C)							
	350	400	450	500	550	650	700	950
	Liquid water content (wt%)							
Piskorz et al. [49] Fluidized bed. SS moisture = 6.23 wt%. Gas residence time = 0.55 s.[a]	22.4	21.1	22.5	24.0	25.2	24.7	32.3	n.r.
Fonts et al. [60] Fluidized bed. SS moisture = 6.7 wt%. Gas residence time in the reactor = ~1 s.	n.r.	n.r.	40.2	n.r.	n.r.	69.7	n.r.	n.r.
Sánchez et al. [92] Fixed bed. SS moisture 6.8 wt%. Long hot-zone residence times.[a]	64	n.r.	58	n.r.	70	n.r.	n.r.	69

[a] Water content calculated from water and liquid yields reported by authors.

appears to be the operational variable with the greatest influence on the liquid water content. Fonts et al. [60] reported that water content can change by 55% within the temperature interval studied (450–650 °C). Besides, the analysis of the data reported by Piskorz et al. [49] also shows that temperature has a greater effect than the other variables analyzed.

Since water may be generated [49,56] and consumed [56] in secondary gas phase reactions, it is assumed that gas residence time also affects the liquid water content. Piskorz et al. [49] and Fonts et al. [60] agree that water content increases with gas residence times. Both the increase in the water yield by possible condensation reactions [49] and the decrease in the organic phase yield by possible gas cracking reactions [49,52,89] favor the increase in the water content with the gas residence time. Piskorz et al. [49] observed a decrease in water content of around 44% when the gas residence time was reduced from 1 to 0.3 s. Fonts et al. [60] observed approximately 20% water content decrement when the gas residence time decreased from 3 to 1 s.

The ash content of the sewage sludge or the presence of ash in the bed also seems to affect the water content. Data reported by Piskorz et al. [49] indicate that the liquid water content reduces around 27% when the sewage sludge has previously had acid extracted and the ash content has been subsequently reduced. Besides, the presence in the bed of a large amount of char and therefore of ash for longer times also provokes an increase in the liquid water content, because this decreases the organics yield and hardly affects the water yield. Considering these results, high ash contents seem to favor higher liquid water contents. In the same manner, Park et al. [89] found that the use of different catalysts (CaO, La_2O_3, CaO/Al_2O_3, La_2O_3/Al_2O_3) in the pyrolysis of sewage sludge causes a slight increase (27–31%) in the water content. However, various other authors have found that the liquid (organic phase) obtained in the catalytic pyrolysis with alumina of the lipids extracted from sewage sludge hardly contains water [76,98,101,110]. In this context, Bahadur et al. [76] determined that the water content of the liquid (organic phase) obtained from sewage sludge lipid pyrolysis with alumina was 0.06 vol%. Although, according to the results obtained by Azuara et al. [110], this fact is due to the better separation of the polar and non-polar pyrolysis liquid compounds into an aqueous and an organic phase.

The aforementioned results suggest that the liquid water content depends on the sewage sludge composition. Several authors have compared the water content obtained with different sewage sludge types [33,46,56,61]. Table 10 shows the liquid water contents obtained with different sewage sludge samples including their moisture and ash contents. Data reported by Pokorna et al. [61] agree with Piskorz et al. [49] about the effect of ash content on water content. The higher the ash content in the sewage sludge, the higher the liquid water content. Fonts et al. [46] agreed with this explanation but also suggested that, apart from the sewage sludge ash content, other aspects of the organic composition such as the quantity of OH groups in the raw sewage sludge sample would also affect the water content. These authors compared two digested sewage sludge samples with different ash content but similar OH group contents and both samples produced similar liquid water contents. However, a third sewage sludge sample with lower ash and OH group contents generated significantly lower water content. This fact is in accordance with the suggestion of some authors that water is produced from dehydration reactions of oxygen-containing compounds in the sewage sludge [56]. Besides, Karayildirim et al. [56] have found that the water contents of liquids from primary sludge is much lower than those from secondary sludge (see Table 10) in spite of the higher moisture and ash content of the primary sludge. Pyrolysis of primary sludge produced lower water yield and higher organic phase yield causing a decrease in the water content. Therefore, pyrolysis of primary sludge also seems to be more appropriate for reducing liquid water content.

Liquid water content is one of the primary criteria recognized by Oasmaa et al. [112] in order to evaluate pyrolysis liquid quality for its use in heat and power applications. These authors recommended liquid water contents between 15 and 25 wt%, and never higher than 30 wt% to avoid heterogeneity and phase separation. The water content of sewage sludge pyrolysis liquid usually exceeds this recommendation. Besides, as has been explained above, water content inferior to 30 wt% for the pyrolysis liquid obtained with sewage sludge also generates phase separation. For this reason, further research work on reducing liquid water content is of interest from the point of view of improving the liquid quality for energetic applications.

Gil-Lalaguna et al. [63] evaluated a selective on-line liquid condensation system equipped with a scrubber and an electrostatic precipitator with the aim of reducing liquid water content. Different operational conditions were tested in the scrubber: washing liquid (water and triethylene glycol), temperature of the washing liquid, volume of the scrubber and temperature of the exit gas flow. The liquids collected in the electrostatic precipitator with the new liquid recovery system showed lower water contents (13–30 wt%) than those collected with the conventional system based on ice condensers (48 wt%). The lowest water content (13%) was achieved when triethylene glycol at 80 °C was used as washing liquid. In spite of the significant reductions in the water contents, the liquids still separated into three phases. For this reason, it is thought that in order to avoid the existence of two organic phases it will also be necessary to modify the composition of the organics of the liquid, since there are organic compounds of very different polarities [63,67].

Table 10
Liquid water content produced from different sewage sludge types.

Reference/most relevant operational conditions	SS type	Moisture content (wt%)	Ash content (wt%)	Liquid water content
Pokorna et al. [61]	Secondary	1.5	25	10.3 ± 1.7 (vol%)
Fixed Bed. 500 °C	Digested	3.7	47.5	78.7 ± 0.3 (vol%)
	Secondary	5.3	27.3	17.0 ± 1.0 (vol%)
Fonts et al. [46]	Digested	6.7	39.9	27.2 ± 2.5 (wt%)
Fluidized bed. 550 °C	Digested	5.3	52.0	44.5 ± 7.7 (wt%)
	Digested	7.1	41.0	46.6 ± 4.2 (wt%)
Karayildirim et al. [56]	Primary[a]	26.3	31.6	32 (wt%)
Fixed bed. 500 °C	Secondary	2.4	20.7	66 (wt%)

[a] Primary sludge from a wastewater treatment plant of a refinery.

4.3.3. Heating value

The heating value of the pyrolysis liquids has been determined by numerous authors, since this property is very important for their application as a fuel [27,33,46,56,60,61,67]. These values are shown in Table 11.

As can be observed, the high heating value of the sewage sludge pyrolysis liquids (or their organic phases) is always higher than 22 MJ kg^{-1}. These values are significantly higher than those of the liquids obtained from lignocellulosic biomass [34]. This is due to the important presence of lipids and extractives in the sewage sludge.

On the other hand, several authors have highlighted the small differences found in the high heating values of their sewage sludge pyrolysis liquids (or of their organic phases) obtained under different operational conditions or from different samples of sewage sludge [33,46,55,60].

Lastly, some authors have determined high heating values over 40 MJ kg^{-1}, which are quite near to those of commercial liquid fuels (45–46 MJ kg^{-1}) [56,67]. Fonts et al. [67] obtained a minority light organic phase with a heating value of 41 MJ kg^{-1}, while Karayildirim et al. [56] determined that the pyrolysis liquids from the secondary sewage sludge of a refinery had a high heating value of 45 MJ kg^{-1}. The extremely elevated high heating value of the liquids produced by Karayildirim et al. [56] is due to the origin of the sewage sludge.

The heating value of the liquids obtained in the catalytic pyrolysis of lipids extracted from sewage sludge using activated alumina was around 46 MJ kg^{-1}, which is comparable to that of diesel fuel, 45–46 MJ kg^{-1} [76]. This is due to the high heating value of the raw material (lipids extracted from the sewage sludge) and also to significant deoxigenation of the liquid when compared to non-catalytic pyrolysis liquid.

4.3.4. Solid content

The solid content of the pyrolysis liquids is an important physicochemical property for its application as fuel. Oasmaa et al. [112] propose that pyrolysis liquids should contain less than 1 wt% and 0.25 wt% of solids for their combustion in diesel engines and turbines, respectively.

However, this variable has not been studied by many authors for sewage sludge pyrolysis liquids [46,60]. In all cases that have been reported, the solid contents are very low (0.033–0.408 wt%), and almost always lower than those proposed by Oasmaa et al. [112]. This is probably due to the composition of the sewage sludge which has a high ash content. For this reason, the solid products of the reaction are particles of a considerable size, and it is therefore difficult for these particles to reach the liquid condensation system swept out by the vapor and gas flow. Furthermore, when sewage sludge is pyrolyzed in a fluidized bed, the solid product is usually eliminated by overflow mode in order to avoid an increase in the bed height during the experiment. In fact, Fonts et al. [60] consider that many of the particles found in sewage sludge liquids are not fines, but carbonaceous particles formed in secondary cracking reactions. Other authors [113] have taken the same view over pyrolysis liquids obtained from lignocellulosic biomass.

4.3.5. Viscosity

The viscosity of pyrolysis liquids is an important physicochemical property because it has a significant effect on the pumping and injecting of a fuel. The viscosity of sewage sludge pyrolysis liquids has been investigated by a limited number of researchers [57,63,67,76,114]. These authors have highlighted different aspects of the viscosity of these pyrolysis liquids. For example, Gil-Lalaguna et al. [63] determined that the viscosities of the two organic phases of their pyrolysis liquids were very different. While the light organic phase had a viscosity around 22 cP at 20 °C, the heavy organic phase viscosity may vary between 400 and 1500 cP. These significant differences are caused by the different compositions of these two phases and probably more specifically by the amount of fatty acids present in the heavy organic phase. In fact, Bahadur et al. [76] claimed that the fatty acids are the compounds that give viscosity to sewage sludge pyrolysis liquids. However, they suggested that the liquid from the catalytic pyrolysis with activated gamma alumina of the lipids extracted from sewage sludge had a viscosity value of only 1.88 cSt due to the catalytic cracking of the fatty acids. As regards the effect of the temperature, Park et al. [57] and Fonts et al. [60] determined that the liquids assumed a more fluent appearance when the temperature at which the reaction took place increased. This is probably due to the cracking of the most viscous liquid components, which is consistent with the reduction of the presence of fatty acids in the liquid when the temperature increases. This decrease in the proportion of fatty acids with the temperature has been found by some authors [91,102]. The evolution with the temperature of the proportion of the different families of the liquid compounds including fatty acids (oxygen-containing compounds) determined by Fonts et al. [91] can be seen in Fig. 4 (Section 4.4.1). Shen and Zhang [114] found that sewage sludge pyrolysis liquids have a lower viscosity than putrescible residue pyrolysis liquids. These authors attributed the low viscosity of the sewage sludge pyrolysis liquid to the high ash content of the sludge which, in the same way as the temperature increase, would cause the cracking of the most viscous liquid components.

4.3.6. pH and ammonia content

Unlike pyrolysis liquids obtained from lignocellulosic biomass, sewage sludge pyrolysis liquids have a basic character [50,55,63]. This is one of the most prominent differences between them. The marked acidity of biomass pyrolysis liquids makes their use as a fuel difficult because of their high corrosive character.

According to these authors, the pH of the aqueous phases of the sludge pyrolysis liquids varies from 8 to 10. The basicity of these liquids is due to the presence of ammonia and nitrogen-containing compounds derived from the protein fraction of the sewage sludge [50,68,76].

Table 11
High heating values of liquid products obtained with different operational conditions and different sewage sludge samples.

Reference/most relevant operational conditions	Kind of sewage sludge	High heating value (MJ kg^{-1})
Inguanzo et al. [27] Fixed bed. 450–850 °C	Digested	22–28 (organic phases in dry basis)
	Secondary	24.7 (oil phase)
Pokorna et al. [61] Fixed bed 500 °C	Digested	27.9 (oil phase)
	Secondary	23.2 (oil phase)
Fonts et al. [60] 450–650 °C	Digested	27–34 (organic phases in dry basis)
	Digested	32 (organic phases in dry basis)
Fonts et al. [46] Fluidized bed 550 °C	Digested	31 (organic phases in dry basis)
	Digested	31 (organic phases in dry basis)
Fonts et al. [67] Fluidized bed 530 °C	Digested	42 (light organic phase)33 (viscous organic phase)
	Primary	36–38
Kim and Parker [33] 250–500 °C	TWAS (thickened waste activated sludge)	37
	Digested	38–39
Karayildirim et al. [56] Fixed bed 500 °C	Primary (from a petrochemical industry)	33
	Secondary (from a refinery)	44

Due to the characteristics of sewage sludge pyrolysis liquids, the pH can only be measured directly in the aqueous phases because of the low water content of the organic phases. In order to determine the acidity or basicity of the organic phases, the pH can be measured from the aqueous fraction extracted with water from these phases [63]. Other procedures to determine the acidity or basicity of the organic phases of the pyrolysis liquids could be the determination of the acid or basic number by means of acid-basic valorizations.

The ammonia content of the sewage sludge pyrolysis liquids was determined by Kaminsky and Kummer [50] and by Azuara et al. [68]. Kaminsky and Kummer [50] determined that the aqueous phase of these liquids obtained between 620 and 750 °C contained an ammonia content of 35–39 g dm^{-3}, while Azuara et al. [68] found that the ammonia content of the liquids obtained at 450 °C, 530 °C and 650 °C was around 28, 22 and 42 g dm^{-3}, respectively.

Due to the high presence of ammonia and nitrogen-containing compounds, the aqueous phase of sewage sludge pyrolysis liquids could be used as a source of chemical compounds for the production of fertilizers [68] or as a source of triacetonamine as was studied by Cao et al. [90].

4.3.7. Oil/tar ratio

The oil/tar ratio can give an idea of the characteristics of the liquid. Oil refers to the light and non-sticky organic compounds in the liquid, while tar describes the heavy, viscous and sticky compounds. From the point of view of fuel application, it is of interest to obtain a liquid with a high oil/tar ratio.

Stammbach et al. [51] and Shen and Zhang [52] investigated the effect of the pyrolysis temperature on the molecular weight distribution of the liquid compounds. Apart from this, Shen and Zhang [52] also studied the effect of the gas residence time. They designated the lighter organic compounds of the liquid (MW < 150) as oil and the heavier ones (MW > 150) as tar. According to the results obtained by these authors, when the pyrolysis temperature increases, the average molecular weight of the organic compounds decreases because of the thermal cracking of the heaviest compounds. In the same way, for longer gas residence times, the proportion of light compounds (oil) increases since these compounds are produced in a higher degree due the thermal cracking reactions of the heavy compounds have more time to occur. Moreover, according to the results obtained by Stammbach et al. [51] the use of a fluid cracking catalyst increases the selectivity to gas and oil by reducing the tar yield.

4.3.8. Ultimate analysis

The elemental composition of a material is crucial to the knowledge of any substance. Table 12 shows elemental analyses

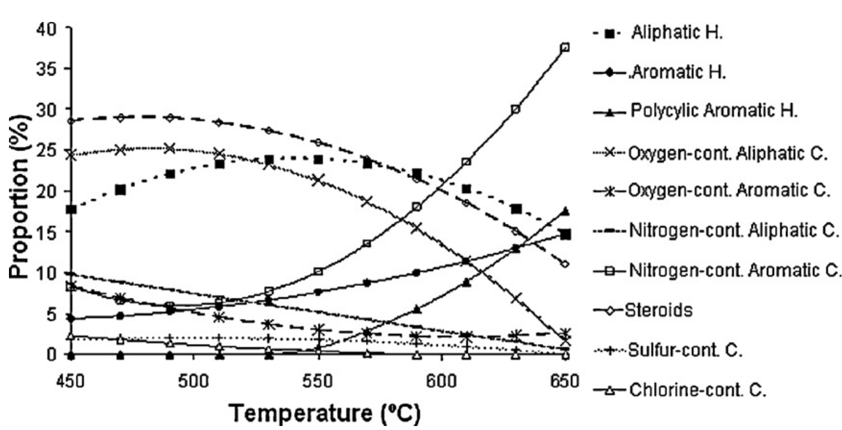


Fig. 4. Evolution of chemical families with the temperature (450–650 °C) [91].

Table 12
Ultimate analyses of sewage sludge pyrolysis liquids and their phases.

References	Characteristic of the pyrolysis liquid sample	C (wt%)	H (wt%)	N (wt%)	O (wt%)	S (wt%)
Konar et al. [101]	Liquid from catalytic pyrolysis with alumina of sewage sludge lipids	86.6	13.5	0.08	0	0.22
Inguanzo et al. [27]	Organic phase	49.4–62.6	9.8–11.5	5.1–5.6	20.4–34.9	0.4–0.6
Karayildirim et al. [56]	Pyrolysis liquid from petrochemical sludge	70.9	10.3	7.5	11.1	0.2
	Pyrolysis liquid from refinery sludge	84.5	12.4	0.7	1.8	0.6
	Pyrolysis liquid from primary sludge	62–74	2.7–8.5	9.5–9.9	8–22	n.r.
Kim and Parker [33]	Pyrolysis liquid from TWAS	63–65	9.4–9.7	6.8–8.5	17–20	n.r.
	Pyrolysis liquid from digested sludge	69–74	9.7–9.9	5.6–6.3	8.4–15	n.r.
Park et al. [57]	Organic phase	36.3–60.8	4.5–9.8	4.2–9.1	24.6–45.7	0.6–1.6
Pokorna et al. [57]	Aqueous phase	69	9.4	6.1	14.3	1.2
	Organic phase	73.4	9.5	8	6.7	2.4
	Light organic phase	75.6	10.5	2.4	11.3	0.2
Fonts et al. [67]	Heavy organic phase	62.2	8.4	8.8	19.6	1
	Aqueous phase	26.6	6.6	7	59	0.8

n.r.: not reported.

(CHNS-O) of sewage sludge pyrolysis liquid or of its phases offered by some authors [27,33,57,61,67].

In general, sewage sludge pyrolysis liquids have greater concentrations of H and C than raw sewage sludge but lower concentrations of N, S and O. The high H and C contents of some of these liquids or phases indicate an elevated heating value. Moreover, sewage sludge pyrolysis liquids have lower O content than pyrolysis liquids obtained from lignocelullosic materials. The high contents in N and S of sewage sludge pyrolysis liquids come from the proteic fraction of the sludge. The nitrogen content of the liquid obtained from the pyrolysis of primary sewage sludge is especially high. The reduction of the nitrogen content of the sewage sludge pyrolysis liquid is an important challenge for the development of this disposal route. Possible ways to solve it that could be studied would be the catalytic pyrolysis, the catalytic treatment of the liquid, the removal of the sewage sludge nitrogen or the fixing of the nitrogen in the solid previously to the pyrolysis reaction.

Table 13 shows the ultimate analyses of liquids obtained in the catalytic pyrolysis of sewage sludge or of its lipids.

The low O, N and S contents of the liquid obtained from catalytic pyrolysis with alumina of sewage sludge lipids should be noted [101]. According to these authors, N and S were reduced by a further 84% in the liquid product with respect to the lipid, while the liquids were virtually free of oxygen. However, it must be taken into account that this catalytic treatment was mainly useful to reduce the O content of the pyrolysis liquids, because N and S were mainly removed (99% rejection) when the lipids were extracted from the rest of the sewage sludge matrix. On the other hand, the liquid fractions obtained by Beckers et al. [99] have an ultimate composition more similar to that obtained in non-catalytic pyrolysis (see Table 12). While taking into account that these authors analyze the composition of the whole liquid, a slight decrease in the N and O contents could be detected.

As can be observed in Table 13, the oil from sewage sludge pyrolysis obtained by Beckers et al. [99] has a huge oxygen content (20.9–30.6 wt%) compared with that obtained by Bahadur et al. [76] (0.0 wt%). These enormous differences could be due to different reasons: the raw material, the kind of catalyst and the procedure to collect the liquid samples. Beckers et al. [99] considered the whole liquid obtained from the catalytic pyrolysis of sewage sludge while Bahadur et al. [76] considered only the organic phase obtained from the catalytic pyrolysis with gamma alumina of the lipids extracted from the sludge.

As regards the nitrogen content, Park et al. [89], investigating the catalytic pyrolysis of sewage sludge in fluidized and fixed bed using CaO, La_2O_3, CaO/Al_2O_3, and La_2O_3/Al_2O_3, observed that the amount of nitrogen compounds did not change with the catalyst utilized.

A few authors have investigated the presence of other elements (Cu, Cr, Pb, Zn, Cd, Ni, Al, As, Ca, Fe, K, Mg, Na, Cl) in sewage sludge pyrolysis liquids [50,51,57,89,115]. According to these authors, most of these elements are hardly volatilized from the raw material during the reaction. After pyrolysis, the solid product contains at least 90 wt% of the total amount of the following elements: Cu, Cr, Pb, Zn, Al, As, Ca, Fe, K and Mg. However, Cd, Na and Cl are volatilized from the sewage sludge to a greater degree. Briddle and Skrypski-Mantele [115] determined that only 65 wt% of the Cd remains in the solid product after pyrolysis at 450 °C, while for Kaminsky and Kummer [50] the percentage of Cd remaining in the solid product obtained at 620 °C was 70 wt%. According to Park et al. [57], around 50 wt% of the total Na is also volatilized during pyrolysis (446–560 °C). However, the results obtained by Park et al. [57] do not indicate that the Na ends up in the liquid product. Lastly, Cl from sewage sludge is volatilized during the pyrolysis reaction and forms HCl and organochlorine compounds [115]. According to Park et al. [89], the liquids obtained from pyrolysis of sewage sludge contain around 498 ppm of Cl, while if the reaction is carried out with a catalyst (CaO, La_2O_3, or a mixture of both), the Cl content is significantly reduced, reaching the highest reduction when the catalyst is used in a fixed bed.

4.3.9. *Toxicity*

Although this property has barely been studied [116–118], it is important to know the toxicity parameters of the pyrolysis liquids for their safe production, handling and storage, and in order to know and control the risks for the population and the environment.

According to Tsai et al. [118], liquid products contain very similar distributions of PAHs and are very rich in naphthene, fluorene, pyrene. These PAH compounds have aroused concerns about the environment and health because some of these compounds present in bio-oils are known to have high carcinogenic potency.

The results of two of these studies showed that over a determined concentration of pyrolysis liquid (15, 20 or 35%), the liquids display mutagenic activity according to the Ames Test [116,117]. Moreover, when the pyrolysis liquid concentration is more than 25%, a toxic effect in *Salmonella typhimurium* is observed. Taking

Table 13
Elemental analyses of sewage sludge pyrolysis liquids and their phases.

References	Characteristic of the pyrolysis liquid sample	C (wt%)	H (wt%)	N (wt%)	O (wt%)	S (wt%)
Bahadur et al. [76]	Organic phase obtained in the catalytic pyrolysis of lipids extracted from sewage sludge	86.6	13.5	0.08	0.0	0.22
Beckers et al. [99]	Liquid fractions from catalytic pyrolysis of sewage sludge with Y-Zeolite	55.0–65.7	8.8–10.0	3.4–5.5	20.9–30.6	n.r.

n.r.: not reported.

into account these results and some other analyses, sewage sludge pyrolysis liquids have been labeled for their acute toxicity, carcinogenic effect, and mutagenic effect by Azuara et al. [116]. According to these authors, in spite of the important effect of temperature and the kind of sewage sludge on the chemical composition, these variables have hardly any effect in terms of these three toxicity parameters.

4.4. Chemical composition of liquid and its phases: influence of various parameters

Sewage sludge pyrolysis liquids consist of compounds of a different nature. These compounds derive from their devolatilization of the sewage sludge (principally moisture and primary pyrolysis products, such as fatty acids, sugars or steroids) or from their formation in secondary reactions of the primary pyrolysis products (reaction water or polycyclic aromatic hydrocarbons).

A detailed study of the sewage sludge liquid composition is not the key point in terms of its utilization as a fuel, but it may be very useful for deepening the sewage sludge pyrolysis pathways and for evaluating the production of valuable chemical products from the sludge.

The chemical composition of sewage sludge pyrolysis liquids has been studied by several authors [46,50,52–55,57,61,67,89–92,102,108,119]. Table 14 shows the aspects of the composition that have been studied and the analytical techniques used for these purposes.

The analytical technique most widely used to analyze the chemical composition of sewage sludge pyrolysis liquids has been gas chromatography coupled with mass spectrometry (GC–MS). Among the chromatographic analyses found in the literature, particularly noteworthy are those carried out by Doshi et al. [108] and Fonts et al. [67], who applied a derivatization technique during the preparation of the sample. This sample pretreatment enables increased resolution of the chromatographic analyses of the compounds with functional groups which contain active hydrogen (—COOH, —OH, —NH and —SH). The gas chromatography analyses carried out by Fullana et al. [119] should also be highlighted because, according to their results, the utilization of multidimensional gas chromatography (MDGC) enables the resolution of the chromatograms to be significantly improved. Some authors have also quantified the amounts of the identified compounds in percentage of area using preferably GC-FID [46,53,54,57,89,91,92,102,108], and a few have done the quantification in mass [50,61,120].

Sewage sludge pyrolysis liquids have also been chemically characterized by Fourier Transform Infrared Spectroscopy (FTIR) [55,61], by Proton Nuclear Magnetic Resonance (H NMR) and by Liquid Chromatography (LC), silica gel fractionation or solvent fractionation [52,67,108,120].

Some authors have analyzed the composition of the whole liquid [46,52,56,89,91,102,119,120] while others have studied only the chemical composition of the organic phase separated from the whole liquid [50,53–55,57,61,67,92,108]. When the chemical composition is analyzed by GC–MS, the results obtained in analyses of the whole liquid and of the organic phase are basically similar if none derivatization technique is used. This can be explained by the fact that most of the compounds detectable by gas chromatography are present in the organic phase. Most of the authors listed in Table 14 found that the sewage sludge pyrolysis liquids contain mainly alkanes, alkenes, aromatic compounds, carboxylic acids, fatty acids, aldehydes, ketones, steroids, fatty nitriles and amides [50,53–57,61,67,91,92,102,108]. Lastly, Cao et al. [120] studied the nitrogen-containing compounds in depth and determined that these compounds were mainly amides, nitriles and nitrogen-heterocyclic compounds. The study of the nitrogen-containing compounds could be interesting from the point of view of choosing a suitable method to reduce the nitrogen in the pyrolysis liquids for their use as fuels.

The H NMR analyses carried out by Shen and Zhang [52] indicated the presence of hydrogen with aliphatic, aromatic and hydroxyl bounds. Pokorna et al. [61] analyzed by FTIR the organic fractions of the liquids obtained in the pyrolysis of non-digested sewage sludge and concluded that these fractions contain mainly compounds with the typical functional groups of the following families: carboxylic acids, amines, amides, nitriles and aliphatic and aromatic structures. It is important to stress that the H NMR and FTIR analyses cannot identify individual compounds by themselves and only characterize the chemical structure of the liquid, assisting other techniques such as GC–MS.

A few authors have applied fractionation techniques in order to classify the compounds of the liquid in different groups according to their polarity [56,67,108,120]. Doshi et al. [108] determined by liquid chromatography that the organic phase of sewage sludge pyrolysis liquids is composed of 11% aliphatic and aromatic compounds, 28% phenols, 28% carboxylic acids and 33% polar compounds. The organic phase of the sewage sludge pyrolysis liquid obtained by Karayildirim et al. [56] was extracted with different solvents and separated into four fractions: asphaltene (16.0%), aliphatic (15.9%), aromatic (23.0%) and polar (41.1%). Similar results were found by Fonts et al. [67] when applying the fractionation solvent scheme to one of the organic phases found in the sewage sludge pyrolysis liquids with 42.6% water soluble compounds and 57.4% water-insoluble compounds, many of them being very apolar compounds (around 29% ≈ 11% over 37.5%). Lastly, Cao et al. [120] fractionated the pyrolysis liquid in 8 fractions of different polarities (from hexane-soluble compounds to methanol-soluble compounds). They determined that the proportion of each one of these groups was between 5 and 15%; that is to say, the liquid contains important amounts of compounds of very diverse polarity.

The chemical composition and the properties of the aqueous phase have been little studied. Only Kaminsky and Kummer [50], Park et al. [57], Fonts et al. [67] and Azuara et al. [68] have offered some data. According to Kaminsky and Kummer [50], the aqueous phase of the sewage sludge pyrolysis liquids contains water, ammonia, methanol, acetonitrile, propanenitrile, pyrrole, pyridine and acetamide. Park et al. [57] determined that the aqueous phase was composed of polar compounds such as

Table 14
Studies about the chemical composition of sewage sludge pyrolysis liquids.

Reference	Studies performed
Kaminsky and Kummer [50]	Effect of the temperature (620–750 °C) on the organic and the aqueous phase chemical composition determined by GC–MS.
Konar et al. [101]	Effect of the catalytic pyrolysis with activated alumina on the composition of the liquid product.
Bahadur et al. [76]	Effect of the catalytic pyrolysis with activated alumina on the composition of the liquid product.
Domínguez et al. [53]	Effect of the kind of sewage sludge (different wastewater purification treatment and different sludge stabilization treatment) and the heating mode (microwave or electric oven) on the organic phase chemical composition determined by GC–MS.
Shen and Zhang [52]	Liquid chemical composition by GC–MS and by H NMR.
Domínguez et al. [54]	Effect of a multimode and a singlemode microwave oven and graphite and char as microwave absorbers on the organic phase chemical compositions determined by GC–MS.
Doshi et al. [108]	Influence of the upgrading treatment (esterification) on the organic phase chemical composition determined by GC–MS and liquid chromatography.
Fullana et al. [119]	Determination of primary and secondary pyrolytic products by multidimensional gas chromatography (MDGC).
Karayildirim et al. [56]	Liquid chemical composition determined by GC–MS.
Domínguez et al. [55]	Organic phase chemical composition determined by FTIR and GC–MS.
Jindarom et al. [102]	Effect of the temperature (350–650 °C) and the atmosphere (N_2–CO_2) on the liquid chemical composition determined by GC–MS.
Park et al. [57]	Effect of the temperature on the organic phase chemical composition determined by GC–MS. Aqueous phase chemical composition determined by GC–MS.
Fonts et al. [91]	Effect of the temperature, the nitrogen flow rate (gas residence time) and the feed rate of solids (solid residence time) on the liquid chemical composition determined by GC–MS.
Fonts et al. [46]	Effect of the kind of sewage sludge (sewage sludge samples anaerobically digested and dry from three different wastewater treatment plants) on the liquid chemical composition determined by GC–MS.
Pokorna et al. [61]	Organic phase chemical composition determined by FTIR and GC–MS.
Sánchez et al. [92]	Effect of temperature on the organic phase chemical composition determined by GC–MS.
Fonts et al. [67]	Composition of the aqueous and the two organic phases of the sewage sludge pyrolysis liquids determined by means of GC–MS and solvent fractionation.
Park et al. [89]	Liquid chemical composition determined by GC–MS.
Cao et al. [120]	Silica-gel fractionation and GC–MS identification of nitrogen species.

tetramethyl-4-pyperidine, 4-amine-4-methyl-2-pentanone and 4-methoxy-N-methylphenylaniline. Fonts et al. [67] determined the same type of compounds as the aforementioned authors and also found carboxylic acids, nitrogen-containing with thiol groups and levoglucosan. As can be seen, most of the aqueous phase compounds contain nitrogen. For this reason, Azuara et al. [68] proposed the utilization of this phase as a fertilizer or as a source for the production of fertilizers.

Apart from the composition of the liquids under certain operational conditions, some studies have reported the effect of these operational conditions on the chemical composition of the sewage sludge pyrolysis liquid. These studies provide information not only about the composition of the liquids but also about the course of the reaction. The most extensively studied operational variable is the temperature [50,57,91,92,102], but other operational variables such as the gas residence time [91], the solid residence time [91], the atmosphere of the reaction [102], the heating mode [54] and the kind of sewage sludge [46] have also been investigated.

4.4.1. *Effect of the temperature*

Some of the cited authors have studied the effect of the temperature on the chemical composition analyzed by GC–MS [50,57,91,92,102]. A summary of their most important findings as regards the effect of the temperature on the different chemical families present in sewage sludge pyrolysis liquids can be seen in Table 15.

Many of these authors agree on the trends identified for the influence of the temperature. According to Kaminsky and Kummer [50], Park et al. [57] and Fonts et al. [91], when the temperature increases the proportion of aromatic hydrocarbons, polycyclic aromatic hydrocarbons and nitrogen containing-aromatic compounds increase. Jindarom et al. [102] and Fonts et al. [91] claim that there is a maximum for the aliphatic hydrocarbons at around 550 °C. Lastly, according to some of these authors the proportion of oxygen-containing aliphatic compounds decreases when the temperature increases [91,92,102]. Fig. 4 shows the evolution of the different chemical families with the temperature [91].

There are few studies about the influence of other operational conditions on the composition of the sewage sludge pyrolysis liquid. The results obtained in these few studies are discussed below.

4.4.2. *Effect of the gas residence time*

According to Fonts et al. [91], the gas residence time has an effect on the compounds that appear or disappear in the secondary gas-phase reactions of the primary pyrolysis products. When the gas residence time increases and the pyrolysis temperature is sufficiently high (500–550 °C), the compounds that derive directly from their devolatilization, such as the extractives, tend to disappear giving rise to more stable compounds such as aromatics, compounds that lose their functional groups or lighter compounds coming from cracking reactions. As mentioned in the section concerning the average molecular weight of the liquid compounds, the increase in the proportion of these lighter compounds when the gas residence time increases was also detected by Shen and Zhang [52].

4.4.3. *Effect of the solid residence time*

These authors studied also the effect of the solid residence time on the liquid chemical composition [91]. According to the results, the effect of the solid feed rate on the composition of the pyrolysis liquids could be related to the catalytic role of the ash contained in the bed material. When the bed material is renewed more quickly (higher solid feed rates due to the material being renovated by overflow), the bed ash is assumed to have a more significant catalytic activity. This catalytic activity affects some families of compounds involved in secondary reactions. As a result, the presence of the polycyclic aromatic hydrocarbons tends to be favored in the liquids obtained at the highest solid feed rates. However, the presence of compounds resulting in the formation of the polycyclic aromatic hydrocarbons, such as aromatic hydrocarbons, increased in the liquids obtained at the lowest solid feed rates studied (higher solid residence times).

4.4.4. *Effect of the reaction atmosphere*

Jindarom et al. [102] studied the effect of carrying out the pyrolysis reaction in two different atmospheres (CO_2 and N_2). The results

Table 15
Summary of the effect of the temperature on the chemical families of the liquid observed by different authors.

Reference	Interval of temperatures studied	Trends observed
Kaminsky and Kummer [50]	620–750 °C	Increase of temperature between 620 and 750 °C causes: Decrease aliphatic hydrocarbons. Increase aromatic and PAH's. Increase oxygen-containing aromatic compounds. Increase nitrogen-containing compounds.
Jindarom et al. [102]	350–650 °C	Increase of temperature between 350 and 650 °C causes: Maximum around 550 °C for the aliphatic hydrocarbons. Increase aromatic hydrocarbons. Decrease oxygen-containing aliphatic compounds. Little effect on nitrogen-containing compounds, steroids, and PAH's.
Park et al. [57]	450–720 °C	Increase of temperature between 350 and 650 °C causes: Decrease aliphatic hydrocarbons. Increase aromatic and PAH's.
Fonts et al. [91]	450–650 °C	Increase of temperature between 350 and 650 °C causes: Maximum around 550 °C for the aliphatic hydrocarbons. Increase aromatic and PAH's. Decrease oxygen-containing aliphatic compounds. Increase nitrogen-containing aromatic compounds. Decrease steroids.
Sánchez et al. [92]	350–950 °C	Increase of temperature between 350 and 650 °C causes: Increase aromatic hydrocarbons. Decrease phenol and its alky derivatives. Maximum around 450 °C for PAH's of 2 or 3 rings. Increase PAH's of 4 or 5 rings. Decrease of oxygen-containing aliphatic compounds.

obtained by these authors show that the proportions of aliphatic and monoaromatic compounds are not significantly affected by the reaction atmosphere. However, they claim that the amount of oxygenated and nitrogenated compounds in the pyrolytic liquid obtained from pyrolysis under CO_2 atmosphere is higher than that obtained from pyrolysis under N_2 atmosphere. The liquids obtained from the pyrolysis under N_2 present a higher proportion of steroids and polycyclic aromatic compounds. According to these authors, the increase of nitrogenated compounds is mainly due to the appearance of a compound (3-carbamic acid methyl ester) that was not detected in those liquids obtained under N_2 atmosphere. Jindarom et al. [102] propose that this compound might be the result of the insertion of CO_2 molecules into the nitrogenated compounds. For this reason, the presence of CO_2 in the reaction atmosphere could promote an increase in the nitrogen content of the liquid, which would be detrimental to its use as a fuel.

4.4.5. Effect of the kind of sewage sludge

According to some authors [46], the composition of the sewage sludge affects the composition of the liquid mainly for two reasons. Firstly, most of the liquid compounds, for example the extractives, come directly from their devolatilization from the sewage sludge. And secondly, the amount and composition of the ash of the sewage sludge also has an effect on the liquid composition, because the metals contained in the ash may catalyze some reactions. Sewage sludge samples with high ash contents would produce liquids with a composition similar to that obtained at higher pyrolysis temperatures [46,91].

In spite of the aforementioned effects of the operational conditions observed in sewage sludge pyrolysis liquids, in general, except the effect of the temperature, they are not very significant. In fact, most of the authors who have studied the liquid composition report the same kinds of compounds.

4.5. By-products of sewage sludge pyrolysis for liquid production

4.5.1. Char

Char is usually the main byproduct of sewage sludge pyrolysis for liquid production. The char yield given in the existing literature varies greatly, usually between 35 and 80 wt%, on a dry basis [27,52,56,58,61]. This is mainly due to the different origins of the sludges and their ash contents.

Other factors, such as the temperature and the solid residence time, have also been identified as influential in the final amount of char after pyrolysis. Increasing temperature causes a steady decrease in char production in all types of reactors [49,58], whereas an increase in the solid residence time in the case of fluidized bed reactors also causes a decrease in char yields [52,58].

The most distinctive feature of sewage sludge chars, if compared to those of lignocellulosic origin, is their high ash content. During pyrolysis, the organic content of chars reduces with increasing temperature, while most of the inorganic content remains in the solid matrix. As commented before, the majority of metals originally contained in sewage sludge remain in the char after pyrolysis, except the volatile elements mercury and cadmium; moreover, heavy metals are more strongly incorporated in the matrix of pyrolysis residue than in the incineration ash or in the sewage sludge itself [50]. XRD and FTIR analyses of chars have revealed the presence of a great number of inorganic compounds such as metal oxides and sulfides, calcium carbonate, alumino-silicates and quartz, amongst others [61,82].

The remaining organic fraction gives a modest porous nature to the chars. The highest values of BET surface area of chars reported from a single pyrolysis step are around 150 $m^2 g^{-1}$ [87].

Chars from sewage sludge pyrolysis are usually of basic nature, with increasing pH at higher pyrolysis temperatures. Some authors have attributed this behavior to the removal of acidic oxygen-containing surface groups from the organic fraction [51]. Ultimate analysis of chars shows that significant amounts of N and S are retained after pyrolysis [61]. Additionally, H/C atomic ratios are found to be low, which has been attributed to the predominance of aromatic structures [49]. This aromatic character is more evident at higher temperatures [82].

The higher heating value of the chars is low, with reported values of 5–21 MJ kg^{-1} [27,33,61,121]. The heating values near to 5 MJ kg^{-1} make it generally unattractive for incineration or any other energetic valorization. However, the energetic valorization of the sludge char products with high heating value could be very interesting [122,123]. In fact, the gasification of char from other biomass fast pyrolysis is also being investigated by some

authors as a route to integrate the whole energetic valorization of a biomass [124–127]. Moreover, the high heavy metal content of chars may require costly treatments for the flue gas. Some authors have pointed out the possibility of landfilling, due to the great solid volume reduction accomplished by pyrolysis that can reach 50% [27,56]. Nevertheless, legal constraints may possibly apply nowadays in the EU. For this reason, other authors advocate the use of sewage sludge chars for adsorbent production. For instance, the aforementioned basic nature of these materials makes them potentially suitable for the removal of pollutants such as H_2S or NOx in gaseous streams [128]. Adsorbent production would require additional chemical or physical steps [27]. Recently, a comprehensive review of the production of sewage sludge adsorbents has been published [32].

Lastly, it is worth remembering that sewage sludge contains phosphorus, which is a scarce and expensive element [129,130]. After sewage sludge combustion, phosphorus concentrates in the ash. Several attempts have been made to recover this phosphorus from the ash obtained from sewage sludge incineration [131–135]. This recovery could be also possible to be carried out in pyrolysis char obtained from wastes like livestock waste [136] or from sewage sludge as it is shown in the study carried out by Bridle and Pritchard [31].

4.5.2. Gas

Like liquid yields, gas yields vary greatly depending on the experimental conditions. Temperature appears to be the most influential parameter. It is generally accepted that an increase in temperature in fluidized bed pyrolysis increases the gas yield, as reported elsewhere [50,52,55,57,58]. High residence times can also provoke substantial variations in the gas yield, because the vapors are able to undergo secondary cracking reactions [55,57]. The catalytic nature of sewage sludge chars may also influence this behavior [46,58]. Reported values for gas yields range within 8–45% (daf) [49–51,61] or 5–30% (sludge basis) [52,56–58].

Similarly to biomass pyrolysis, the main compounds detected in sewage sludge pyrolysis gas are CO, CO_2, CH_4, H_2 and light hydrocarbons. According to Shen et al. [52], all these compounds are increasingly generated with increasing temperatures, with the exception of CO. Some authors have also identified a wide range of hydrocarbons (up to C6) [56]. Due to the nature of sewage sludge, a remarkable feature is generally the high concentration of H_2S in the pyrolysis gas [46,56]. Traces of other compounds, such as N_2O and carbonyl sulfide, have also been reported [49,52].

Also depending on the parameters mentioned, reported heating values of the gas vary between 5 and 36 MJ kg^{-1} [49,50,52,55,57,58,61]. Some authors propose using pyrolysis gas to provide heat for the pyrolysis process itself [58] or running it autothermally, and even for drying part of the sewage sludge [51]. Nevertheless, one of the main drawbacks for this final use of the gas would be the potentially high amounts of H_2S as the main gas pollutant.

4.6. Applicability of the process

Various studies propose different applications for sewage sludge pyrolysis liquid. However, experience of the applicability of the sewage sludge pyrolysis process at pilot or commercial scale remains limited.

As regards lab-scale researches into liquid applications, various applications have been proposed. For example, Fonts et al. [67] suggested that the light organic phase rich in hydrocarbons, steroids and triglycerides that they obtained in the pyrolysis of sewage sludge could be co-combusted with diesel and biodiesel, because this phase contained numerous compounds highly soluble in these fuels. Furthermore, they proposed combustion of the heavy organic phase in lime kilns due to its high viscosity and nitrogen content. According to Azuara et al. [68], the aqueous phase of the liquid could be used as a fertilizer directly or as a source for producing fertilizers. As regards the production of valuable chemical products, Cao et al. [90] used a reactive condensation system with acetone to produce triacetonamine, which is useful as an intermediate for the synthesis of pharmaceutical products, pesticides and photostabilizers for polymers. Triacetonamine was obtained as a result of the reaction between the acetone and the ammonia produced in the sewage sludge pyrolysis reaction.

To the best of the authors' knowledge, Enersludge^{TM} or Oil-from-Sludge (OFS) technology is the only industrial application of sewage sludge pyrolysis for liquid production [137]. Based on this technology, the Water Corporation of Western Australia awarded a contract to the ESI-Clough Joint Venture (ECJV) in November 1996 to design, construct and operate the first commercial-scale facility world-wide [138]. This first plant was built in Perth (Australia) for treating the raw primary sludge (RPS) and the waste activated sludge (TEAS) generated at the Subiaco wastewater treatment plant, which at that moment amounted to between 15 and 18 dry tpd.

The main processing operations of this plant included the dewatering, the drying and the pyrolysis reaction of sewage sludge, the refining of the vapors, the recuperation of the energy contained in the by-products of the reaction (char, non-condensable gases and reaction water) and the cleaning of the gases [31,103,104,115,138]. In this plant, sewage sludge was fed to the pyrolysis reactor in the form of pellets with 5% moisture. The pyrolysis reaction takes place at 450 °C and at 1.5 kPa (g). From this reaction two products were obtained: a solid called char and a gas called "raw gas". These two products were re-contacted again in a second reactor, also operating at 450 °C, in order to refine the compounds of the crude gas to give hydrocarbons. The char was used as catalyst since it inherently contains the catalysts (aluminum silicates and heavy metals) needed for the refining reaction. The vapors obtained are condensed by means of direct contact with a spray of the cooled aqueous phase, also called reaction water. Oil and reaction water were separated in an oil–water separator. The three low grade fuels obtained in the reaction (char, reaction water and non-condensable gases) were combusted in order to produce the energy needed for drying the sludge in the Hot Gas Generator (HGG). A diagram of this plant is shown in Fig. 5.

According to the data shown by the authors, this process enables all of the sewage sludge energy to be recovered in its four pyrolysis products, principally in the oil (45%) and the char (40%). The oil produced (over 300 tonnes) was exported off-site and successfully combusted by industrial users, mainly in boilers for steam generation. The authors [138] state that the operational experience of the Subiaco plant has clearly demonstrated the energy and environmental benefits offered by the technology. Not only does the process provide all the energy needed for sludge drying, but it also achieves a net export of 7 GJ/t of processed sludge, improved control of heavy metals and extremely low air emissions [138]. Moreover, the char contained significant amounts of N and P that can be recovered to be used as source of nutrients in agriculture [31].

According to Bridle and Unkovich [138], the positive aspects obtained from the experience gained during the operation of this plant are that the oil has been successfully combusted by industrial users, the conversion reactor has performed extremely well, the issues relating to solid/gas handling systems downstream of the reactors have been resolved satisfactorily and, above all, as commented, the operational experience has proved the energy and environmental benefits of the process. However, this plant is not currently in operation. The authors explained the critical factors for optimal operation of the plant. One of them is the impact of the variable sludge properties on the dewatering, the drying and the HGG.

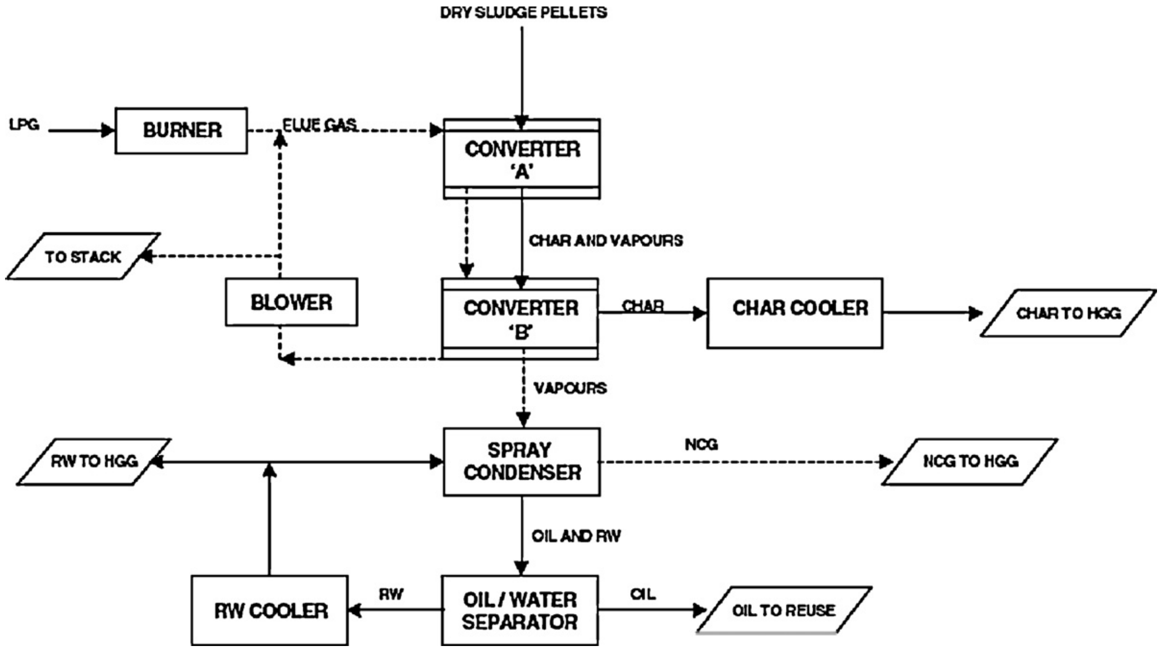


Fig. 5. Flow diagram of the Enersludge™ pyrolysis plant located in Perth (Australia) [31].

The sludge properties of major importance are the raw primary sludge (RPS) to waste activated sludge (TEAS) ratio (RPS/TEAS), the phosphorus content, the hair and fiber content and the oil grease content. If the bulk density of the pellets is lower than 400 kg m^{-3} or if the sewage sludge has a high phosphorus content, many different problems may arise in the HGG. From an energy perspective the preferred feed stock is raw sludge, because the energy output from processing raw sludge is three times that gained from processing digested sewage sludge. However, from a process stability point of view, the digested sludge option is decisively more secure. Another critical factor is the design and the integration of the equipment, due to the novelty of the process. The maintenance of the plant and the control of odor emissions were more difficult and costly than expected.

Lastly, according to these and other authors, full scale implementation of the pyrolysis of sewage sludge has been limited by the low economic value of the liquid produced and the relative complexity of the processing equipment [31,33,115]. According to Bridle and Unkovich [138], pyrolysis would be a more competitive treatment if the oil price exceeds a certain value, 30 ¢/L at that moment (2004). On the other hand, according to the economic evaluation carried out by Kim and Parker [33], the largest economic benefit (using the product liquid as fuel) would be produced if primary sludge was pyrolyzed at 500 °C. To sum up, the economic viability of the process may be improved if the liquid yield is enhanced, if the cost of fossil-derived fuels increases more and/or if value-added products can be produced from the pyrolysis by-products, such as adsorbents from the solids, fertilizers from the aqueous fraction and syn-gas from the gas [33,61].

5. Conclusions

Pyrolysis of sewage sludge for liquid production has been widely studied by a considerable number of researchers. The studies show that the liquid yield may vary between 27 and 54 wt% on sewage sludge fed basis or 51 and 80 wt% on dry ash free (daf) basis. The liquid yield and its physicochemical properties depend mainly on the operational conditions and on the composition of the sewage sludge. The temperature is the most influential operational condition. According to the results reviewed, a temperature value between 450 and 550 °C maximizes the liquid yield and/or the organic phase yield. An increase in the temperature in the ranges studied also causes a change in the composition of the liquid, obtaining a liquid product with a greater proportion of aromatic and polycyclic aromatic compounds, a lower proportion of oxygen-containing aliphatic compounds and steroids, and usually higher water contents. This change in the composition leads to a decrease in the liquid viscosity. The heating value, however, is less affected by the operational conditions. Other conditions such as the gas and the solid residence times, the sewage sludge particle size, the reaction atmosphere or the condensation system also have an effect on the yield and properties of the liquid, but the effect is less significant.

The sewage sludge composition (moisture, ash and extractives) has an important influence on the pyrolysis process for liquid production. For this purpose, sewage sludge samples with low water contents, low ash contents and high extractive contents are of interest. High ash content in sewage sludge seems to favor the cracking of the pyrolysis vapors produced in the reaction and a consequent decrease in the liquid yield and increase in the gas yield. Sewage sludge samples with low water contents are of interest because all the moisture from the sewage sludge ends up in the liquid product, unless a selective condensation system is used. High ash contents in sewage sludge could lead to a decrease in the liquid yield, an increase in the water content, a lower liquid viscosity and a liquid with a higher proportion of aromatic and non-substituted compounds. On the other hand, most of the extractives from sewage sludge appear in the liquid obtained after the pyrolysis reaction. These extractives usually contribute positively to the heating values of the pyrolysis liquids, although they cause an increase in viscosity and a separated phase rich in extractives if no catalyst is used.

Sewage sludge pyrolysis liquid usually separates into two or even three phases. Most researchers have found two phases (aqueous and organic) although some have identified two differentiated organic phases (a light and a viscous one) and one aqueous phase.

The main applications proposed for the organic phases are as fuels, either alone or by means of blending with diesel or biodiesel. Some of their properties could, however, be improved. In order to enhance their quality, catalytic treatments should be used. For

example, the on-line reforming of sewage sludge pyrolysis vapors could lower the viscosity and increase the heating value of the organic phase, as well as enable a better and easier separation of the aqueous and organic phases. Moreover, it seems that these treatments do not reduce the yield to the organic phase. On the other hand, the high nitrogen content of the aqueous phase suggests it may be used as a fertilizer or as a source for the production of fertilizers or other valuable chemical products such as triacetonamine.

Catalytic pyrolysis of sewage sludge seems to improve the characteristics of the organic phase for use as a fuel: increasing the hydrogen to carbon ratio, increasing the heating value and decreasing the oxygen to carbon ratio and the viscosity. However, from the point of view of the authors, efforts should be invested in the reduction of the liquid nitrogen content, since this represents a very important limitation to its use as fuel.

Lastly, although the only industrial sewage sludge pyrolysis plant operated to date is currently closed, it is worth reconsidering this management option due to the lack of energy sources (fossil fuels or nuclear resources) and to the lack of clear strategies available for managing this waste. These two factors may stimulate efforts to find solutions for handling sewage sludge by means of pyrolysis and for the production of a liquid that could be used as a fuel or as a source of chemically valuable products.

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